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Proton Nuclear Magnetic Resonance (H NMR) of Glycolate in Real Waste:

Developing and Testing Analytical Methods for the Savannah River Site Liquid Waste System

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PREFACE OR ACKNOWLEDGEMENTS

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EXECUTIVE SUMMARY

In preparation for implementing the Nitric-Glycolic (NG) acid flowsheet for the Savannah River Site (SRS) Liquid Waste System (LWS), analytical methods for determining glycolate at low concentration, below 10 mg/L in radioactive samples, are requested to support system management and safety. Previously, Savannah River National Laboratory (SRNL) developed, tested, and deployed an ion chromatography (IC) method which performed well for samples with low to moderate ionic strength. That previous work also included a scoping effort to determine if an alternate analytical strategy using proton nuclear magnetic resonance (H NMR) would complement and extend the capabilities of the IC method. Use of H NMR for quantitative analysis, in this case to quantify glycolate at low concentrations in liquid waste, was an SRNL innovation. The H NMR scoping results were promising, indicating that the method could expand SRNL's capabilities for glycolate analysis in LWS samples to higher ionic strength tanks/solutions.

SRNL has now developed, refined, and demonstrated the H NMR method for glycolate analysis in high ionic strength LWS tank solutions, such as those that feed the 2H and 3H Evaporators for quantifying glycolate and identifying select other organic solutes. This method uses a sample preparation protocol to lower sample dose and activity by stripping Cs and Sr from the samples. This step also removes other radioactive and paramagnetic elements leading to safer sample handling and improved sensitivity. Additionally, the sample viscosity is lowered by pH adjustment increasing signal sensitivity. Several variants of the H NMR method were developed and tested (providing a range of target sensitivities). In the most sensitive variants, samples are pH adjusted with nitric acid in heavy water (D_2O) to below 0.1 M total base and undergo multiple crystalline silicotitanate (CST)/monosodium titanate (MST) strikes with filtration through a polyethersulfone (PES) filter. Use of D_2O enables the instrument to overcome magnetic drift, termed instrument lock, supporting a high number of scans per sample. Using the locked strategy for Tank 38, a Limit of Detection (LOD) of 1 mg/L with a Limit of Quantitation (LOQ) of 5 mg/L was achieved in a concentrated sample from the 2H Evaporator system. Similar results were observed for Tank 22.

SRNL also demonstrated the NMR method may also be applied to identify and quantify other organic compounds in high ionic strength solutions. Analysis of simulated 6 M Na waste samples containing varying concentrations of methanol were analyzed by NMR and an LOQ of 6 mg/L and LOD of 2 mg/L were determined. The simulated waste was selected as a challenging matrix for methanol determination and the results indicated the methodology has applicability to real waste samples.

The H NMR method for analysis of glycolate is a scientific advancement that provides a viable tool for characterizing LWS samples. The research demonstrated that the method extends the capabilities of SRNL to quantify glycolate to a wider range of LWS conditions with increased sensitivity compared with IC. The expanded portfolio of methods, including both IC and H NMR, provides more options to engineers for characterizing, understanding, and managing the flowsheet and LWS operations. For low to moderated ionic strength samples with glycolate concentrations at 10 to 50 mg/L, IC provides data more rapidly and at a lower cost. H NMR provides the capability to analyze higher ionic strength solutions and similar sensitivity when analyzed without the D_2O lock. The H NMR method provides an improvement in sensitivity when performed using the D_2O lock, longer run times, and standard addition protocols. Prior to deployment of this method for glycolic acid flowsheet transition samples, procedures will need to be developed and finalized.

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LIST OF ABBREVIATIONS

AMP	Ammonium molybdophosphate-polyacrylonitrile
CN	cellulose nitrate
CPC	Chemical Processing Cell
Cs	cesium
CSSX	Caustic side solvent extraction
CST	crystalline silicotitanate
CSTF	Concentration, Storage, and Transfer Facilities
CU	containment unit
D_2O	Heavy Water
DSA	Documented Safety Analysis
DWPF	Defense Waste Processing Facility
EDTA	Ethylenediaminetetraacetic acid
H NMR	proton Nuclear Magnetic Resonance
IC	ion chromatography
ICP ES	Inductively Coupled Plasma Emission Spectroscopy
IEC	International Electrotechnical Commission
ISO	International Organization for Standardization
LOD	limit of detection
LOQ	limit of quantitation
LWS	Liquid Waste System
MST	monosodium titanate
NG	Nitric-glycolic acid
NIST	National Institute of Standards and Technology
NMR	Nuclear Magnetic Resonance
PES	Polyethersulfone
QA	Quality Assurance
RCT	Recycle Collection Tank
SAM	Standard Addition Method
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
S/N	signal to noise ratio
Sr	strontium
TTQAP	Task Technical and Quality Assurance Plan
TTR	Technical Task Request
WATERGATE	Water Suppression by Gradient Tailored Excitation

1.0 Introduction

1.1 Scope and Background

In preparation for implementing the NG acid flowsheet for the SRS LWS, analytical methods for determining glycolate at low concentration are desired to support system management and safety. Previous work documented that the IC method performed well for samples with low to moderate ionic strength.[1] That work also included a scoping effort to determine if an alternate analytical strategy using H NMR would complement and extend the capabilities of the IC method. The H NMR scoping results indicated that the method had the potential to expand glycolate analysis in LWS samples to higher ionic strength tanks/solutions. The scope of this work is to develop innovative proton NMR techniques, including demonstrating ion exchange decontamination protocols needed for application of the technique to real waste samples.

Part of radioactive waste processing at SRS uses formic acid to reduce oxidized (Hg^{2+}) to more volatile elemental Hg for steam striping, collecting, and disposal. Under acidic conditions found in the Chemical Processing Cell (CPC) at the Defense Waste Processing Facility (DWPF), formic acid has a much higher hydrogen generation rate than an alternative reductant, glycolic acid.[2] Thus, an NG acid flowsheet has been developed utilizing glycolic acid with the benefit of easing the need for headspace monitoring requirements for hydrogen and ammonia at DWPF. Low concentrations of glycolate are conservatively assumed to be in the recycle stream, which will collect in the Recycle Collection Tank (RCT). The DWPF recycle stream collected in the RCT has a distinct pathway to the LWS waste tanks that feed the 2H and 3H Evaporator. This route involves transfer of the DWPF recycle to Tank 22 in the Concentration, Storage, and Transfer Facilities (CSTF) followed by transfer to the LWS tank farm/evaporators (Figure 1-1).

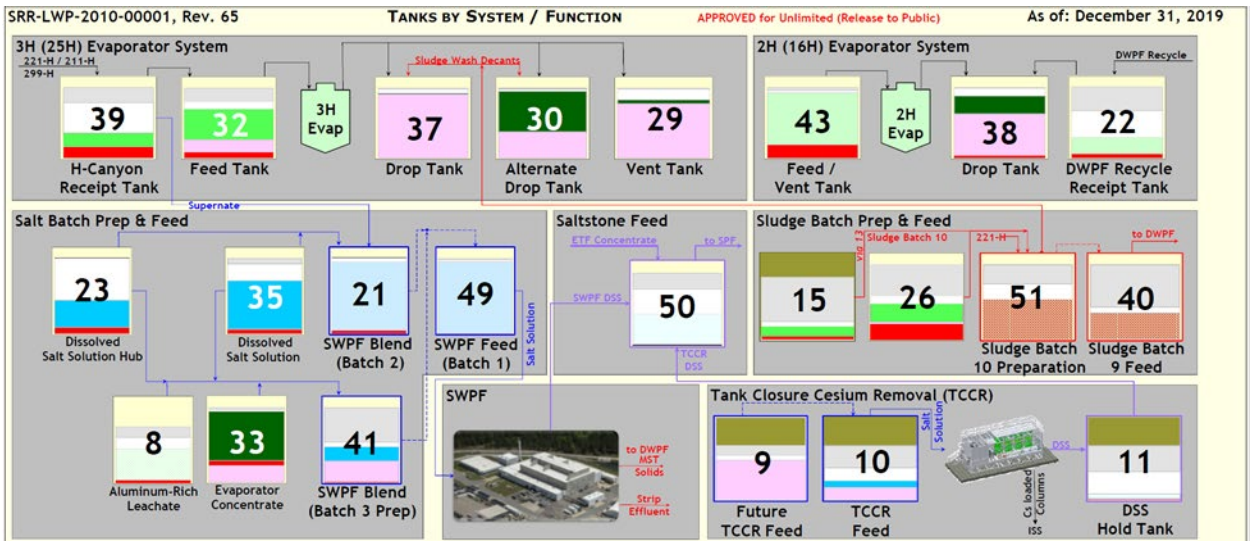

Figure 1-1: Tanks Feeding the 2H and 3H Evaporators

Under caustic tank waste conditions, researchers at SRNL demonstrated thermolytic degradation of glycolate leading to the evolution of hydrogen not seen with formic acid.[3] A permanganate oxidation process has been developed to treat and reduce the concentration of glycolate in the recycle stream prior to transfer the CSTF. Analytical techniques for the determination of glycolate in low mg/L concentrations are required to support the NG acid flowsheet.

There is a desire to decrease detection limits for glycolate in high ionic strength samples from the tanks feeding the 2H and 3H Evaporators as driven by the Documented Safety Analysis (DSA) under development for the Tank Farm. H NMR is a useful tool to verify the presence of carboxylic acid compounds in water. Several literature articles[4] from the food industry use this method to identify and quantify carboxylic acids. The SRNL has successfully used this analytical method[1] on low dose (6E07 dpm/mL Cs-137) radioactive condensate returned to Tank 22 with no sample dilution during glycolate measurements for DWPF. The protocol to be used uses 1) CST/ MST strikes to lower the dose rate, 2) standard addition method (SAM) using glycolate,[5] and 3) H NMR analysis to identify organic compounds (e.g. methanol, glycolate, aromatics, etc.) and quantify glycolate. The H NMR experiment relies on Water Suppression by Gradient Tailor Excitation (WATERGATE)[6] to suppress a large water signal in the spectrum. An LOQ was determined for 2H or 3H Evaporator high ionic strength feed tanks based on the SAM method as described by the Task Technical and Quality Assurance Plan (TTQAP) with a Functional Classification of Safety Class[7].

1.2 Analytical Strategy and Explanation

Samples from many of the tanks that feed the 2H and 3H Evaporators (Figure 1-1) require their dose rate and activity lowered for safe handling when analyzing by H NMR. Measurable concentrations of glycolate are not expected to be currently present in the tanks feeding the 2H and 3H Evaporator since the NG acid flowsheet has not been implemented at DWPF[8]. Thus, a split sample strategy using glycolate spikes of known concentration was used to confirm the H NMR method could correctly identify and quantify glycolate in tank waste. Each tank sample received in the Shielded Cells was equally portioned into aliquots with various concentration levels of glycolate added and an internal standard. Samples analyzed by the NMR need to be free of solids for optimal field homogeneity and low in viscosity (~1 CPS) for maximum resolution. Samples were batch treated with titanate ion-exchangers[9] (CST and/or MST) and filtered to remove the main contributors to dose rate, cesium and strontium. Additionally, paramagnetic elements, actinides, and lanthanides, were removed. The final solution was particle free and low in activity. Figure 1-2 shows the general strategy used where steps in the yellow box occur in the cells and steps in the green box occur in a containment unit (CU). Figures 3-16, 3-18, and 3-21 in the report contain more details that arose as the method was developed. These details include number of titanate strikes to lower dose rate, pH adjustments to lower viscosity and improve cesium decontamination factors, addition of D_2O to prevent magnet drift, and addition of an internal standard to track sample dilution.

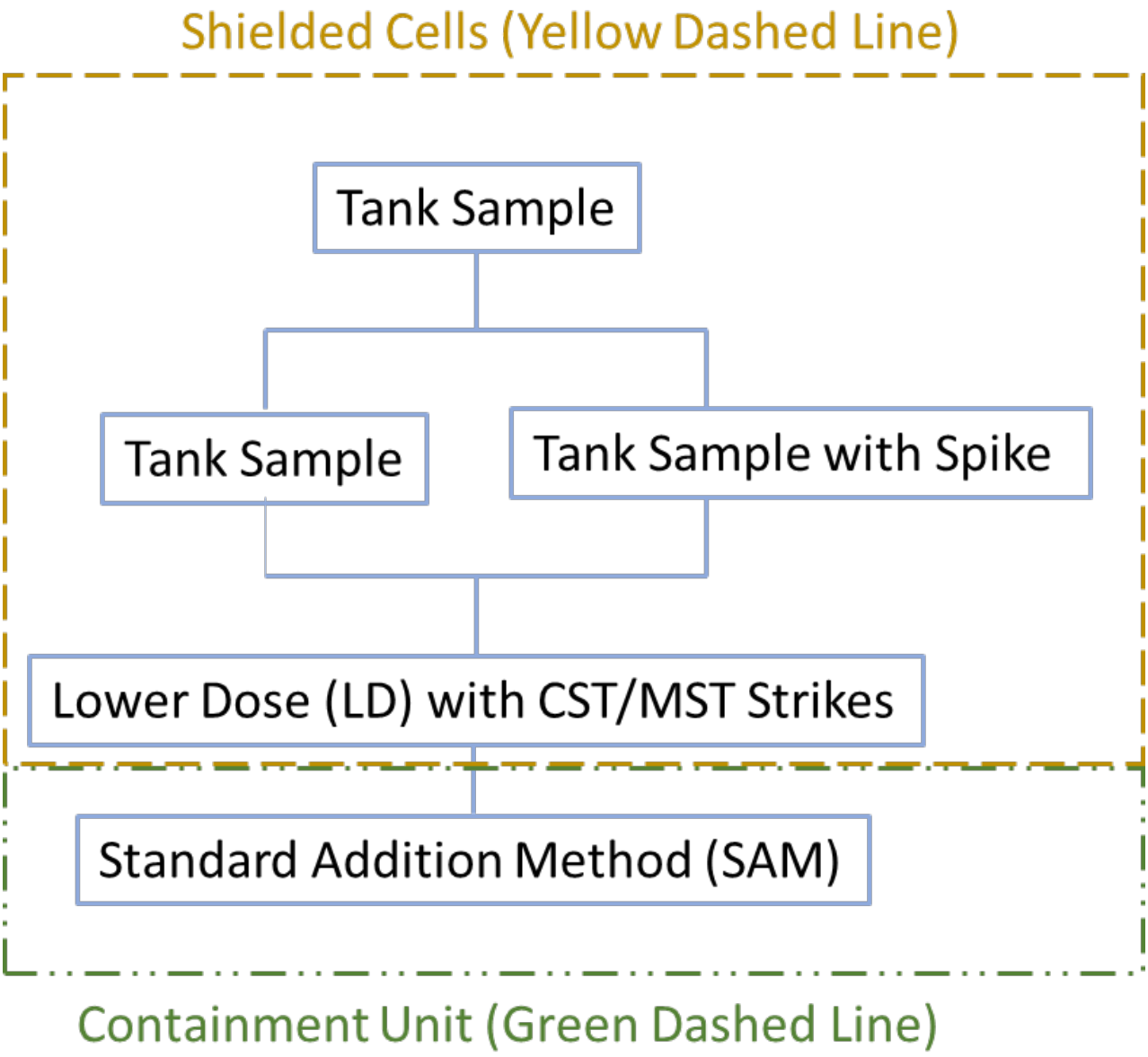

Figure 1-2: Sample Preparation Strategy for H NMR Analysis

To quantify glycolate, four samples for H NMR analysis are generated from the one tank sample using the standard addition method[5] (SAM). Glycolate is spiked into three of the samples in increasing concentration, the four samples are analyzed for glycolate, and the peak heights are graphed (peak height vs spike amount). The output of a hypothetical SAM quantification is shown in Figure 1-3 where linear regression is used to determine the glycolate concentration at the x-axis. The sample/spike table describes the concentrations of the spikes. Peak heights corresponding to the nuclear spin relaxation resonance of the hydrogens (Figure 1-3) on the glycolate molecule are plotted versus the concentration of the spike (mg/L) added. The value at the x-axis is negative and reported as an absolute value in mg/L. The 2-sigma error is where the green error line intersects the x-axis above and below the x-axis concentration estimate.

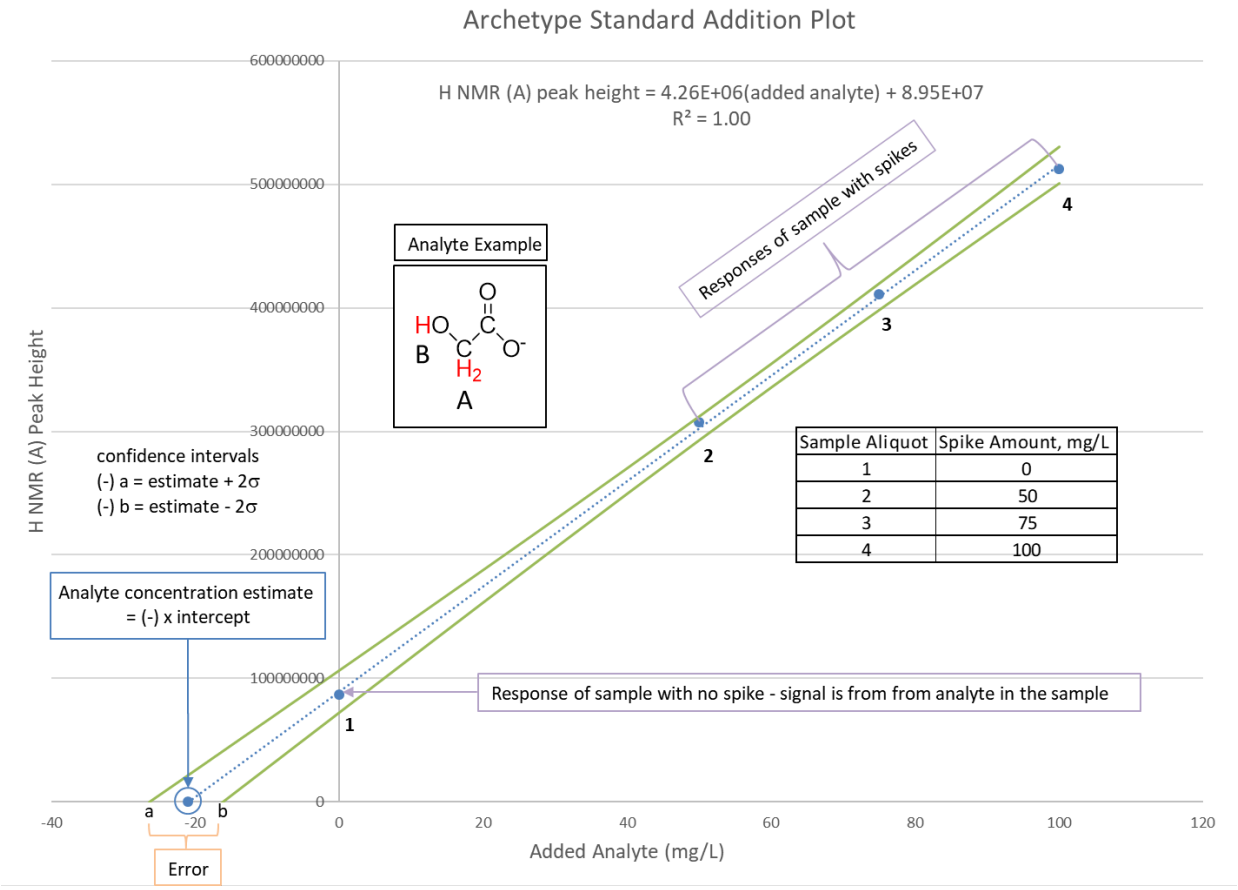

Figure 1-3: Archetype Standard Addition Method Plot

1.3 Glycolate

Glycolic acid is a two-carbon alpha hydroxy carboxylic acid that exists as glycolate in caustic tank waste as shown in Figure 1-4. The (red) hydrogens are observed at 3.95 ppm as a singlet and quantified by measuring the peak height on the H NMR spectrum. The reported pKa of the carboxylic acid is 3.8[10] in water and will be slightly lower in high ionic strength solutions (up to 0.5 pKa units lower).[11] The two methylene hydrogens (pKa > 25)[12] and the hydrogen attached to the alcohol (pKa > 15) are visible in the H NMR. The weak acid compound exists as a single anion in alkaline tank waste (pH~14). Glycolate is highly soluble in basic solution and is expected to remain soluble in the tank waste supernate. Solids and high viscosity can interfere with optimal H NMR analyses, so each sample was filtered (0.45-micron filter) and diluted or pH adjusted as necessary.

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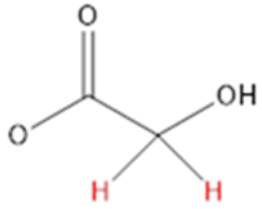

Figure 1-4: Glycolate Form Under Basic Conditions with the Two Protons Used to Quantify by H NMR in Red

2.0 Experimental Procedure

This study was initiated through a Technical Task Request (TTR)[7a]/TTQAP[7b] with a Functional Classification of Safety Class. The work and documentation were performed in a manner compliant with Quality Assurance (QA) requirements. Requirements for performing reviews of technical reports and the extent of review are established in Manual E7 2.60[13]. For SRNL documents, the extent and type of review was accomplished using the SRNL Technical Report Design Checklist.[14] Records for this work are contained in electronic notebook.[15] Throughout this document glycolate and glycolic acid are used where glycolate exists in basic solutions and glycolic acid exists in acidic solutions. For instance, the eluent used for the IC analysis is basic KOH and the analyte exists as glycolate. The pedigree of the glycolate standards used was International Organization for Standardization (ISO) Guide 34, ISO/International Electrotechnical Commission (IEC) 17025 and Certified to ISO 9001 National Institute of Standards and Technology (NIST) traceable.

2.1 Summary Simulant and Waste Tanks Examined

This section lists the simulated waste and the tank samples analyzed. The SAM H NMR method was demonstrated on the 6 M Simulated Waste described in Table 2-1 using methanol and glycolate. The glycolate was also examined in 1 M, 2 M, 3 M, 4 M, and 5 M Na waste simulant to determine sensitivity. Several tank samples were examined to develop a useable analytical protocol by scrutinizing the ramification of the filter media/titanate, pH adjustments, and D_2O locking compound addition on glycolate quantification. Tank samples examined are shown in Table 2-2.

Table 2-1: 6 M Simulated Waste Used for Initial Testing

Analyte	Molarity (M)	Analyte	Molarity (M)
Na^+	6.29	AlO_2^-	0.245
K^+	0.0150	$C_2O_4^{2-}$	7.97E-03
Cs^+ (cold)	4.28E-04	PO_4^{3-}	7.03E-03
Zn^{2+}	1.18E-04	MoO_4^{2-}	8.37E-05
Sr^{2+}	9.95E-05	NO_3^-	2.21
Cu^{2+}	2.56E-05	NO_2^-	0.600
Sn^{2+}	1.95E-05	Cl^-	2.94E-02
Free OH	2.46	SO_4^{2-}	0.164
CO_3^{2-}	0.180	F^-	3.37E-02
Density	1.2494 g/mL		

Table 2-2: Tanks Examined

Tank	Identifier	Matrix	Na, M	OH, M	Total base, M	Density, g/mL
22	HTF-22-20-69	Caustic Supernate	*0.6 estimate*	0.13	*0.15 estimate*	1.03
22	HTF-22-20-91	Caustic Supernate	*0.6 estimate*	0.13	*0.15 estimate*	1.03
30	HTF-30-20-32	Caustic Supernate	14.9	9.38	10.1	1.52
32	HTF-32-20-29	Caustic Supernate	13.3	7.37	8.21	1.49
37	HTF-37-20-25	Caustic Supernate	13.2	7.35	8.03	1.50
37	HTF-37-20-26	Caustic Supernate	13.4	7.31	7.47	1.50
37	HTF-37-20-90	Caustic Supernate	9.26	4.01	4.87	1.38
38	HTF-38-20-62	Caustic Supernate	4.24	1.29	1.79	1.18
38	HTF-38-20-103	Caustic Supernate	2.83	0.69	1.07	1.14
38	HTF-38-20-104	Caustic Supernate	7.24	2.31	3.19	1.35

2.2 Bruker 300 MHz Ultrashield AVANCE Spectrometer

A 1.5 mL of filtered (0.45 micron) waste or simulant sample is pipetted into a Sigma-Aldrich Norell Select Series 5 mm NMR tube maintaining the outside of the tube contamination free. The tube is securely capped and then loaded into the top of the NMR magnet for analysis (left item in Figure 2-1). For a SAM analysis, all four samples are analyzed in succession with the magnet unlocked. The H NMR experiment WATERGATE (Water Suppression by Gradient Tailored Excitation) was applied to suppress the large water signal at 5.1 ppm in the aqueous samples. This method relies on applying a gradient spin echo technique to separate the water magnetization (by diffusing it with two gradients) from other signals[6a]. A hard 90-degree pulse is applied to magnetize the water followed by a 2 ms gradient pulse (a sine-shaped gradient of 50 mT/m was applied to diffuse it). Lastly, a train of pulses set at different angles acts as a 180-degree pulse for everything else in the sample except for water. The delay between the pulses was 355 µs, the spectral width was 72,000Hz, and the time domain was 8K data points (the acquisition time was 56 ms). Figure 2-1 is a photograph of the instrumentation used.

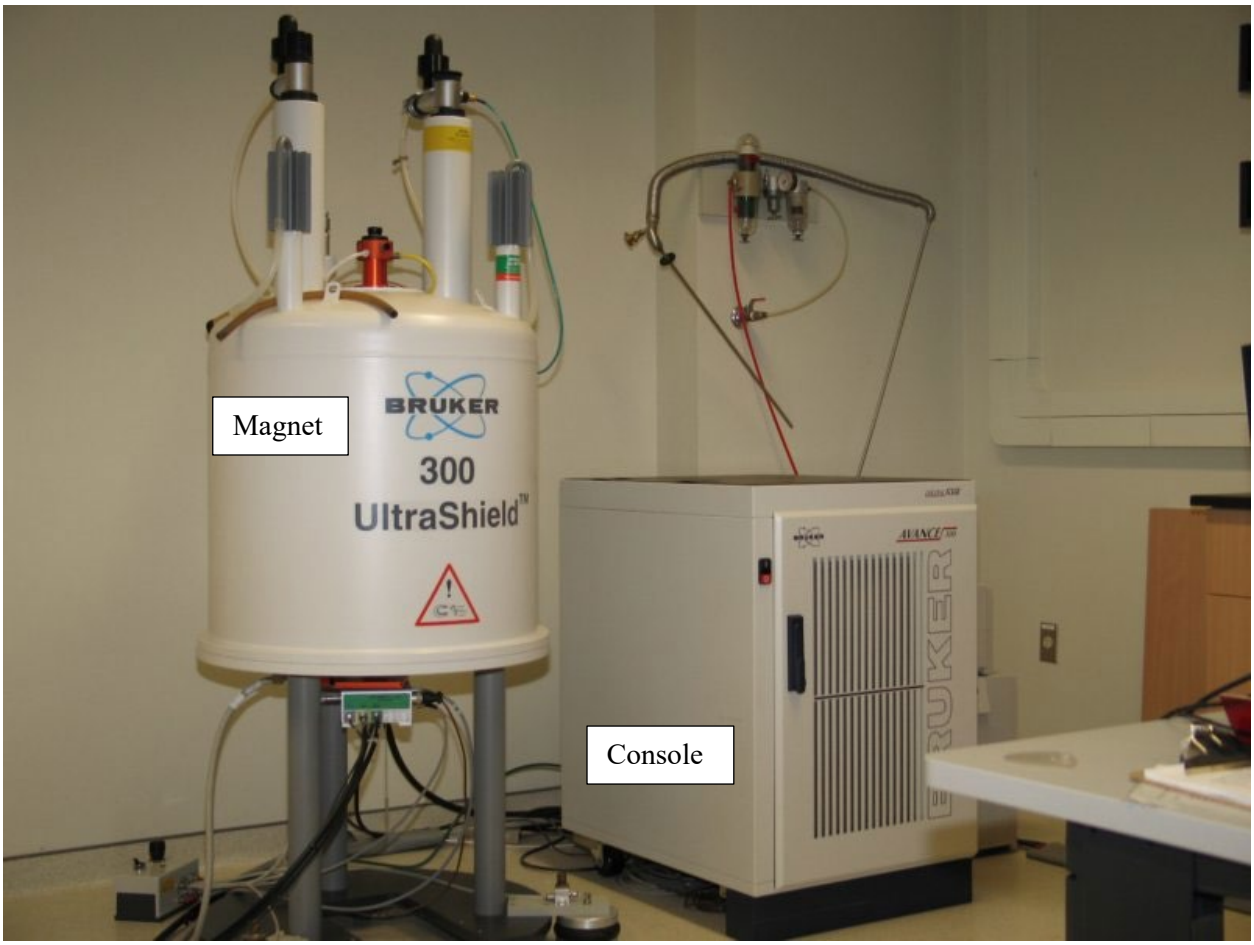

Figure 2-1: Example of Bruker 300 MHz Ultrashield Avance NMR Spectrometer with the Magnet on the Left and the Console on the Right

2.3 Scoping Studies in Simulated Waste

Prior to Shielded Cells work, the caustic, high ionic strength simulated waste shown in Table 2-1 was utilized to test and improve the H NMR method through scoping studies. Appendix A contains the Research and Development directions for testing 1) SAM of a non-chelating analyte methanol, 2) SAM of glycolate, 3) intensity of the glycolate peak versus hydroxide molarity, and 4) metal removal strategies that could chelate glycolate including ethylenediaminetetraacetic acid (EDTA) strike, Biotage silica thiol strike, and OnGuard II H^+ cartridge treatment. This work demonstrated an initial LOQ near 50 mg/L.

2.4 General Ion Exchange Strike Protocol

Appendix C describes the CST/MST strike protocol used for each tank. This protocol was most effective when the total base of the sample was lowered to below 0.1 M closely matching the total base concentration in Tank 22. Figure 2-2 is the sample treatment performed to obtain the final sample contained in an H NMR tube ready for analysis. Samples above 0.5 M total base are adjusted to below 0.1 M with nitric acid and D_2O (15%v/v). At this lower base concentration, the CST/MST strike more effectively removes 1) Cs and Sr, 2) actinides and lanthanides, and 3) paramagnetic elements such as iron. Safe handling practices are met with treated samples exhibiting a lower dose rate and activity. Additionally, removing paramagnetic elements benefits H NMR sensitivity for glycolate.

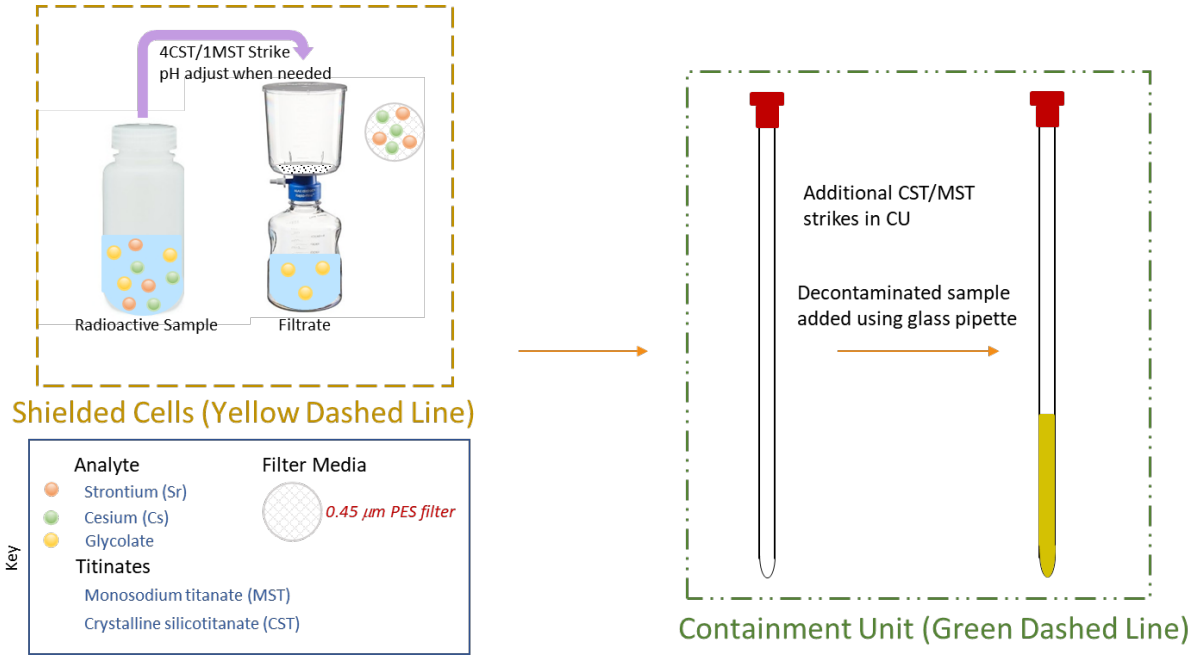

Figure 2-2: Schematic of Ion Exchange Treatment of Tank Waste Samples

2.5 Glycolate in LWS samples

The SAM data generated by the H NMR is contained in Appendix D for radioactive waste samples. Samples from tanks with total base above 1 M (Table 2-2) such as Tanks 30, 32, 37, and 38 were pH adjusted to below 0.1 M with nitric acid while Tank 22 (near 0.1 M) was not pH adjusted. D_2O was added as a locking agent to samples intended for long analysis times. Figure 2-3 is a legend of how the samples were analyzed and will be used throughout the report. Internal standard was added to each sample as a means of ensuring correct dilutions. Initially, acetic acid was used but H NMR analysis of caustic blanks showed acetate present as an impurity. The internal standard was then changed to benzilic acid.

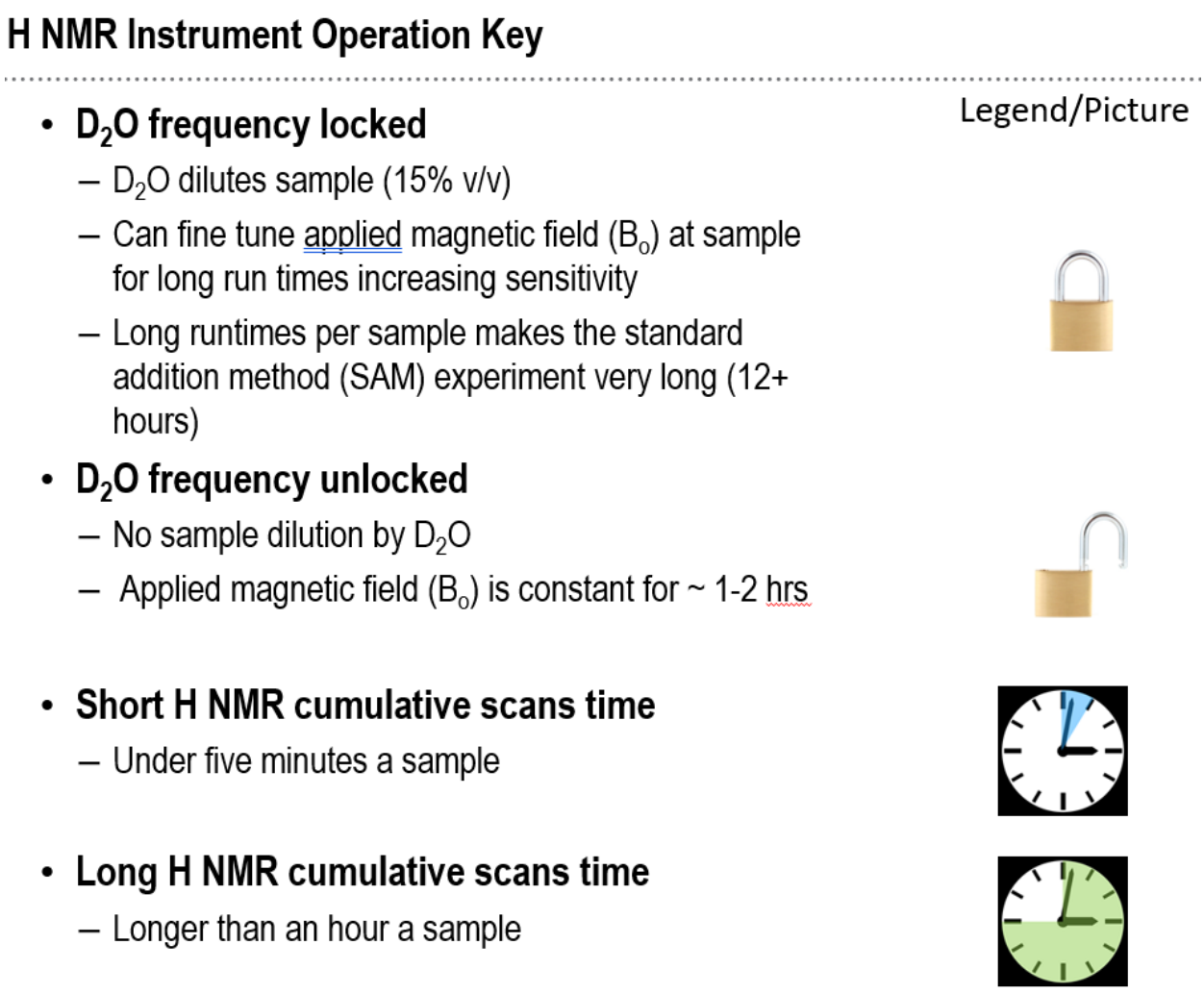

Figure 2-3: Operation Variables of H NMR Experiments

3.0 Results and Discussion

Glycolate has been observed in Hanford waste tanks where the complexant was disposed (8.8×10^5 kg) and, to a much lesser extent, generated in-tank from the aging of other complexants[16]. Tank waste samples are generally analyzed using IC[17] with water dilution. SRS waste tanks have not received glycolate from on-site processing[18] but do receive formate. IC is used at SRS to quantify glycolate in tank waste solutions. IC performs well for solutions with low to moderate ionic strength, such as samples from Tank 22, providing practical quantitation limits in the range of 5 to 10 mg/L. However, high ionic strength degrades the IC peak shape and necessitates higher sample dilution and lower sensitivity. The IC detection limits for samples from the tanks feeding the 2H and 3H Evaporators are generally 500 mg/L and higher due to high concentrations of nitrate and required dilution factors.[1] Figure 3-1 visually explains the dilemma with high nitrate concentration leading to a large peak that interferes with the glycolate peak. To correct the problem, samples need to be diluted to a point that the interference is minimized, raising the detection limit. Nitrate lacks hydrogen atoms and does not appear in the H NMR spectrum. The invisible nature of the high concentration anions and cations to H NMR analysis is the scientific basis of the H NMR method and prompted the testing and development of this analytical tool for glycolate determination.

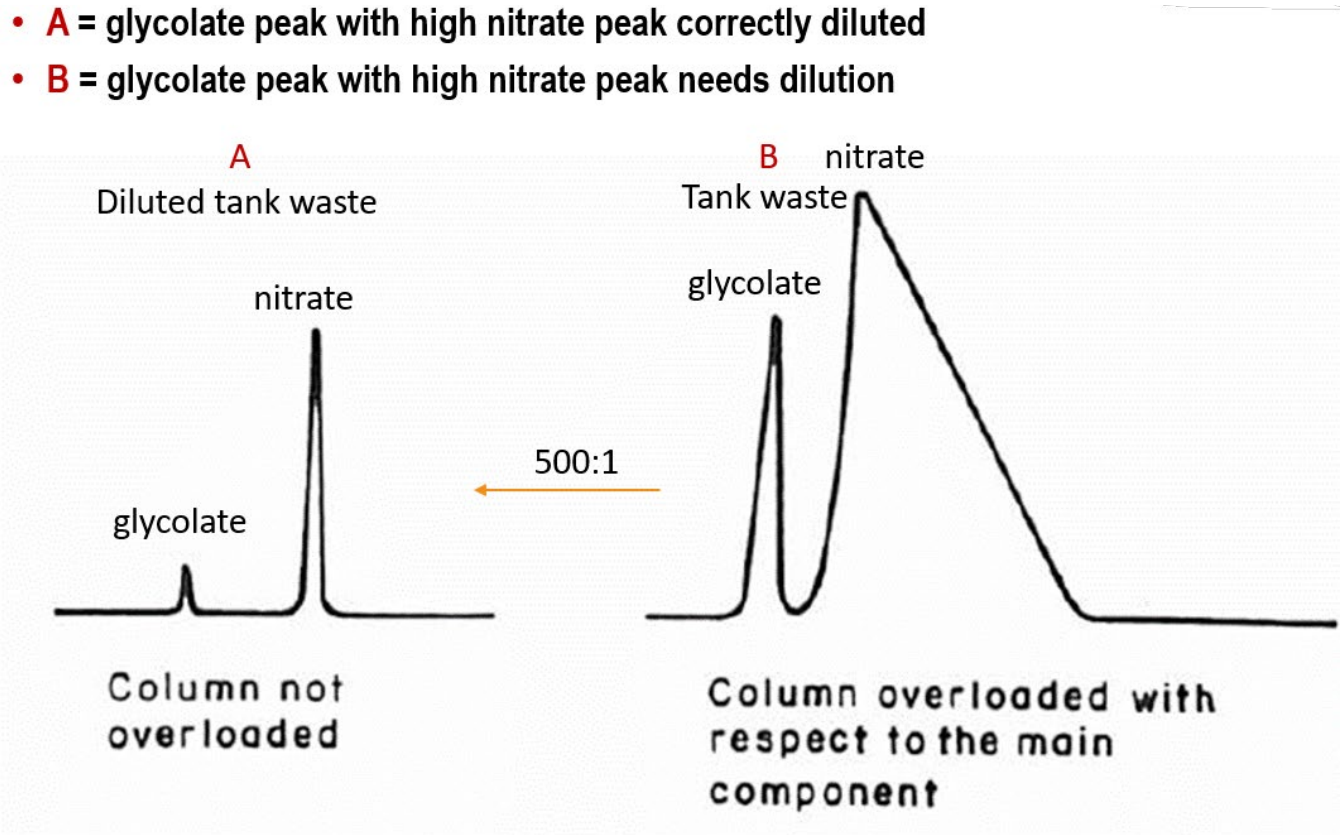

Figure 3-1: Visual Demonstration of the Need to Dilute (500:1) High Nitrate Concentration Tank Samples[19]

Initial scoping use of the H NMR method for glycolate analysis targeted a sample from the SRS tank farm, Tank 22, that was relatively low in ionic strength, dose rate (Cs 6E07 dpm/mL), and hydroxide (>0.1 M). This work[1] showed glycolate could be detected in an undiluted Tank 22 solution to an LOQ of 10 mg/L. The work in this report applies the H NMR analytical protocol to SRS tank farm samples that are higher in ionic strength, dose rate, and hydroxide concentration while attempting to maintain a similar LOQ. Several issues can potentially affect the sensitivity of the analysis for glycolate such as 1) chelation preventing free rotation of the glycolate molecule[20], 2) viscosity, 3) solids, and 4) dose rate. Figure 3-2 shows two examples of how glycolate chelates a metal preventing free rotation of the molecule and broadening the H NMR signal.

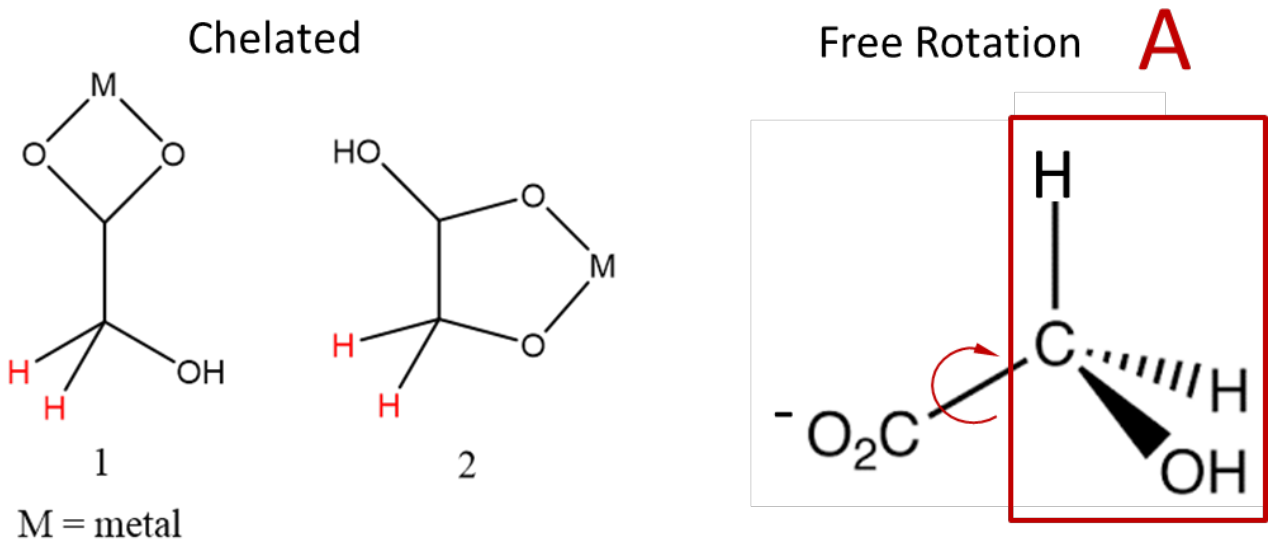

Figure 3-2: Examples of Glycolate Chelating a Metal Preventing Free Rotation of the Sigma Bonds (Box A Contains Two Observable Hydrogens)

3.1 Use of H NMR as a Scanning Tool

The H NMR can be used to scan for other organics leading to the identification of other compounds if they are present. Figure 3-3 shows several hydrogen-containing functional groups that would be visible at single digit mg/L concentrations if present in the sample. A Tank 37 spectrum is shown at the top of the figure as an example where prominent peaks have been identified. The spectrum is compared to a blank sample of similar hydroxide concentration to ensure impurities from processing are identified.

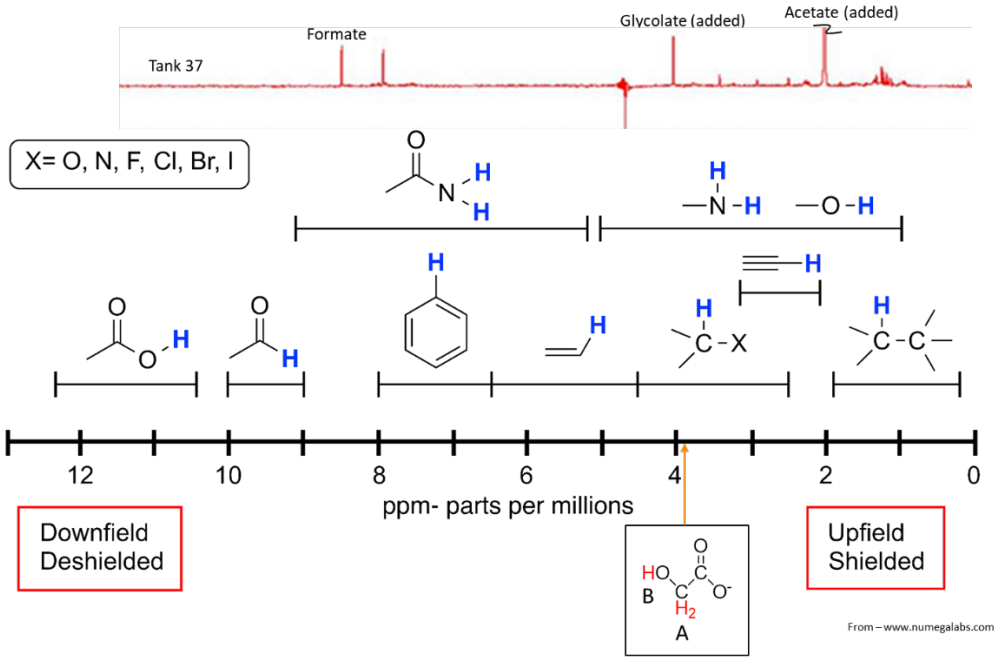

Figure 3-3: H NMR Used as a Screening Tool for Identifying Hydrogen Containing Compounds by Functional Group

3.2 High Ionic Strength Simulant Spiked with 50 mg/L Glycolate

Samples high in viscosity and solids can affect relaxation times[21] for H NMR (t_1 and t_2) and lower sensitivity for compound quantification. Care is taken to ensure solids are not present during sample analysis. Figure 3-4 shows the overlay of five H NMR spectra where glycolate is present at 50 mg/L. As the hydroxide concentration decreases, the signal to noise of the CH_2 signal from glycolate increases due to a decrease in solution viscosity. Examples of NaOH, KOH, HCl, and KCl from the literature[22] are shown to the right of the H NMR spectra where these four compounds increase the viscosity of the solution as they increase in concentration. This phenomenon poses an issue when trying to quantify glycolate in the range of 1 to 10 mg/L. A standard addition method (SAM) was tested on a waste simulant (2.46 M OH, 6 M Na) higher in hydroxide concentration than previously tested Tank 22 H (~0.5 M OH) using the same concentration of glycolate spikes (10, 25 and 50 mg/L). The peak height of glycolate spikes of 25 and 10 mg/L could not be discerned causing the SAM to fail. Based on this data, a pH adjustment protocol was developed to lower the viscosity of high ionic strength tank waste samples (<0.5 M OH).

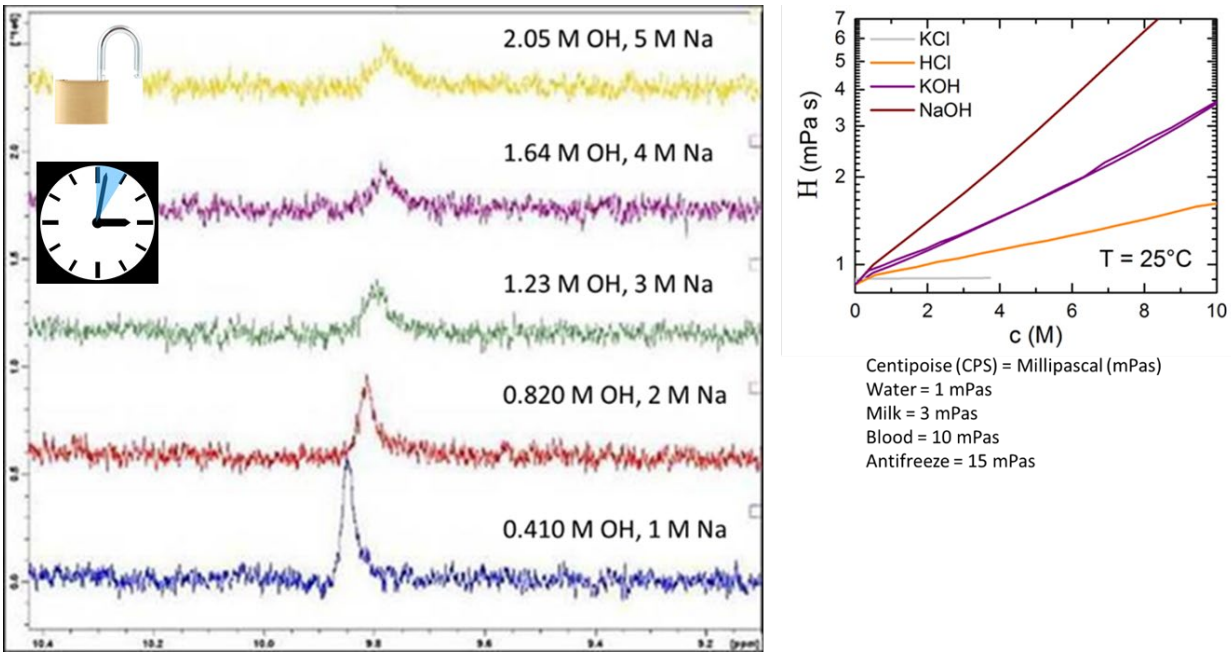

Figure 3-4: Unlocked H NMR Spectra Showing Glycolate at 50 mg/L in Simulated Waste Increasing in Sensitivity as the Hydroxide Concentration and Viscosity Decrease with Dilution

Chelation of the glycolate complexant impacted sensitivity. A series of scoping experiments were performed on the waste simulant to improve signal to noise. Two strategies, (1) temperature and (2) cation removals/chelation, were investigated to prevent complexation from inhibiting free rotation of the atoms in glycolate. Each NMR spectrum was compared to the original spectrum of a 50 mg/L glycolate waste simulant prior to applying the treatment strategy. An H NMR sample tube containing 50 mg/L glycolate in simulated waste was heated and cooled to examine temperature effects. Useful signal-to-noise ratio (S/N) improvement was not observed. Additionally, pretreatment of the simulated waste sample (50 mg/L glycolate) with Agilent 2.5 cc OnGuard II H^+ cartridges, Biotage Silica Thiol (60 mg in 2 mL), and Ethylenediaminetetraacetic acid (EDTA; 25 mg in 2 mL) followed by H NMR analysis showed no significant improvement.

3.3 Methanol Analysis

When 50 mg/L of methanol was analyzed in the same waste simulant used for the glycolate testing, the sensitivity remained relatively high compared to glycolate (Figure 3-5). There are likely a number of reasons for this difference; mainly, 1) methanol is not a complexant allowing for free rotation of the molecule in viscous solutions, 2) methanol has three protons instead of two protons, and 3) methanol (MW = 32 g/mol) molecular weight is about half as heavy as glycolate (MW = 76 g/mol) so approximately twice as many methanol molecules are present for the same mg/L concentration. Linear regression was used to determine a LOQ of 6.63 mg/L and an LOD of 2.19 mg/L as shown in Appendix B.

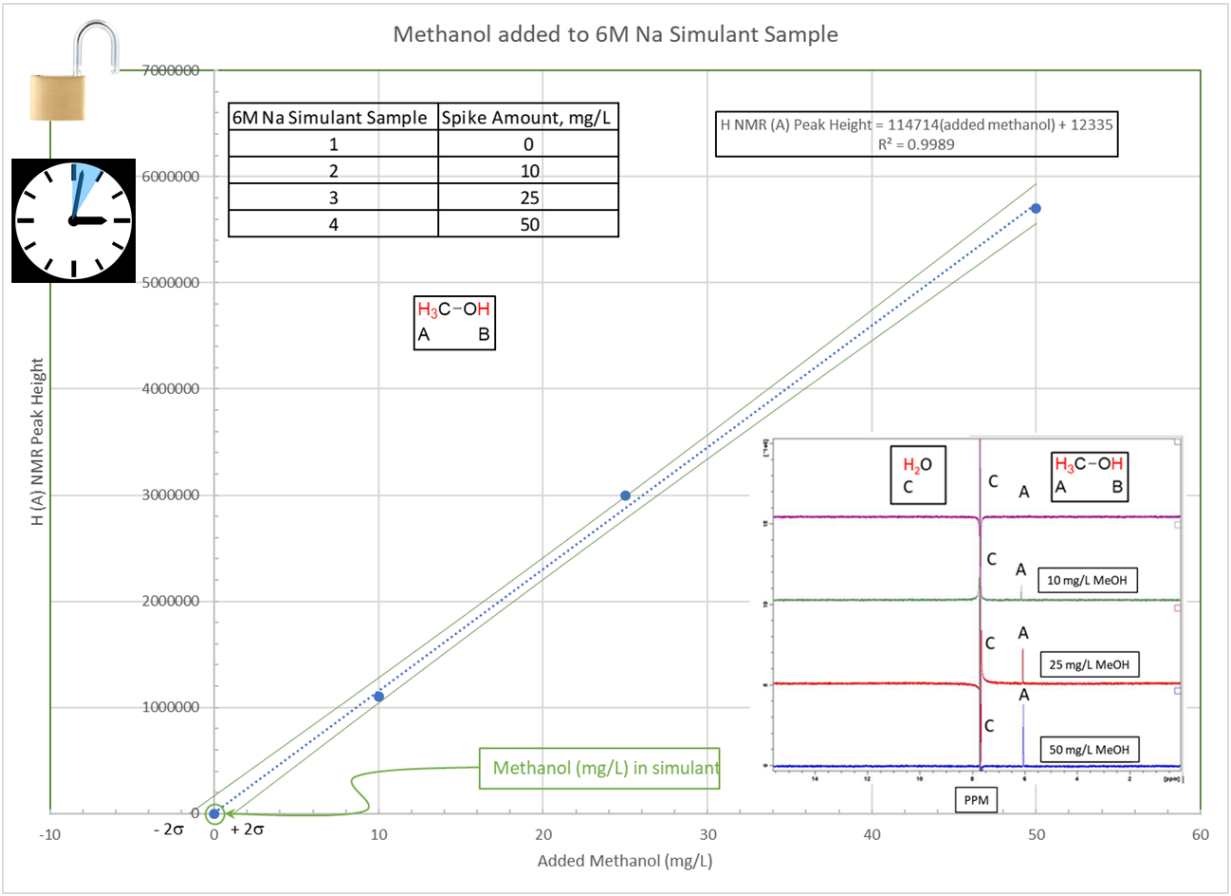

Figure 3-5: Unlocked H NMR Analysis of Waste Simulant (2.46 M OH, 6 M Na) Spiked with Three Concentrations of Glycolate (Scans = 16, 12 Seconds a Scan)

3.4 Titanite Ion Exchange Media used to Lower Dose Rate and Activity of H NMR Samples

Radioactive tank waste requires the removal of Cs-137 and Sr-90 to significantly lower the dose rate and radioactivity for safe sample handling at the NMR instrument. Both MST for Sr-90 and other metals, and CST for Cs-137/Sr-90 have successfully been used to remove these radionuclides[23] from strongly alkaline salt solutions.[24] Using CST and MST in tandem is very effective[23b] and became the final protocol used to decontaminate radioactive samples after initial scoping testing. Other decontamination methodologies including the use of Caustic Side Solvent Extraction (CSSX) solvent, resorcinol/formaldehyde resin, zeolite, and Ammonium molybdophosphate-polyacrylonitrile (AMP) were a less viable option. These alternative methodologies had the potential to introduce organic impurities and/or would not effectively decontaminate cesium under alkaline conditions. The titanate results are summarized in Appendix C and Figure 3-6 highlights the improved decontamination of Cs and Sr after pH adjustment (red bars) to lower a hydroxide

concentration like Tank 22 (~0.1M OH green bar). Additionally, these ion exchange titanates will remove actinides, lanthanides, and paramagnetic elements like iron III. Technetium 99 is not affected by the treatment.

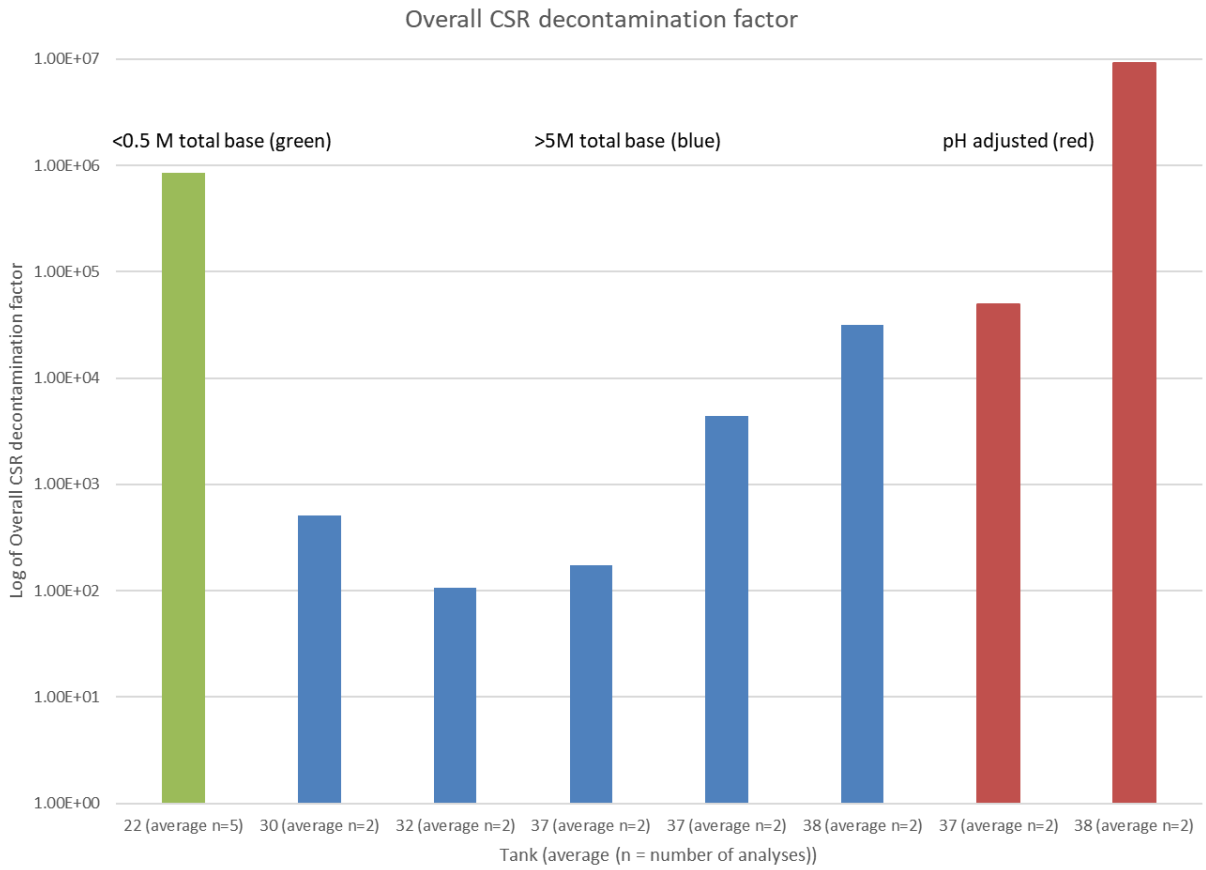

Figure 3-6: Plot of Cesium Removal (CSR) Decontamination Factor on Various Evaporator Feed Tanks

3.5 Development of High Ionic Strength Sample Preparation Protocol – Concerns with Filtration Media and Number of NMR Scans

SRNL personnel identified two resolvable issues with the analytical protocol that were 1) choice of the correct filter media and 2) loss of magnetic drift during long NMR scan times. Initial analysis of Tank 37 samples (HTF-37-20-25) showed impurities in the samples and blank (3 M NaOH treated the same as a sample with titanate strikes) using the protocol shown in Figure 1-2. The large response in the Tank 37 H NMR spectrum between 3.0 and 4.5 ppm in Figure 3-7 shows numerous compounds that interfere with the glycolate peak at 3.9 ppm. These compounds were not observed in the Tank 22 H spectrum which has a hydroxide concentration near 0.1 M while Tank 37 the hydroxide concentration was near 6 M, which was diluted 1 to 4 (1.5 M) prior to titanate strikes and filtration. The Tank 37 hydroxide solution caused degradation of the cellulose nitrate (CN) filter media.

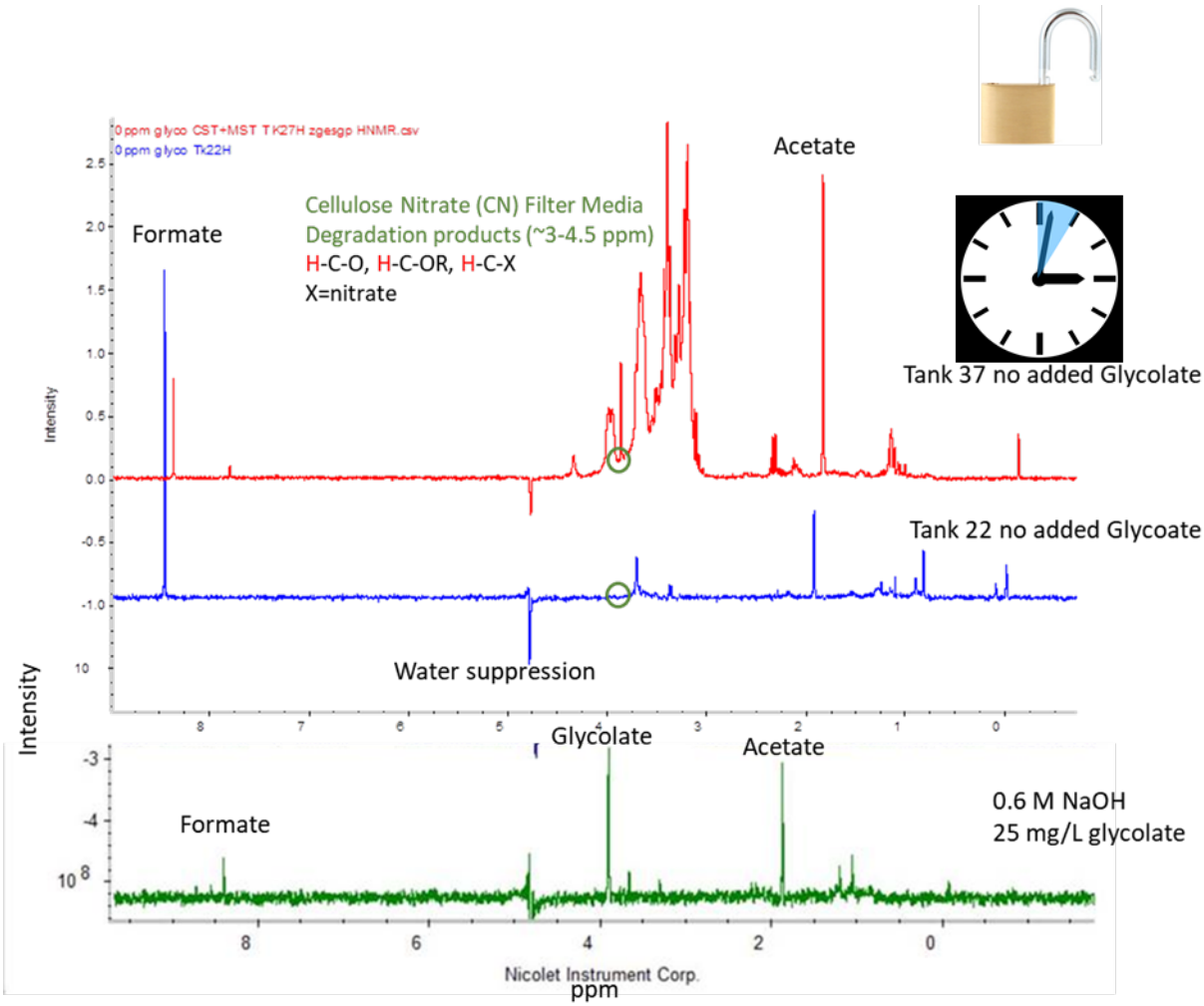

Figure 3-7: Tank 37, Tank 22, and a Control Filtered Through Cellulose Nitrate Filter Media - the Green Circles Show no Interference in Tank 22 and Interference in Tank 37

CN and nylon filter media were exposed to varying concentration of NaOH as shown in Figure 3-8. Degradation of the CN occurred especially at high concentrations (>1 M) of hydroxide leading to a noisy baseline. Nylon showed no interference at 3.9 ppm where the glycolate CH_2 shows a response under varied caustic conditions. Similarly, polyethersulfone (PES) filter media also showed no interference at 3.9 ppm when tested under caustic conditions and was the filter chosen for the final analytical protocol.

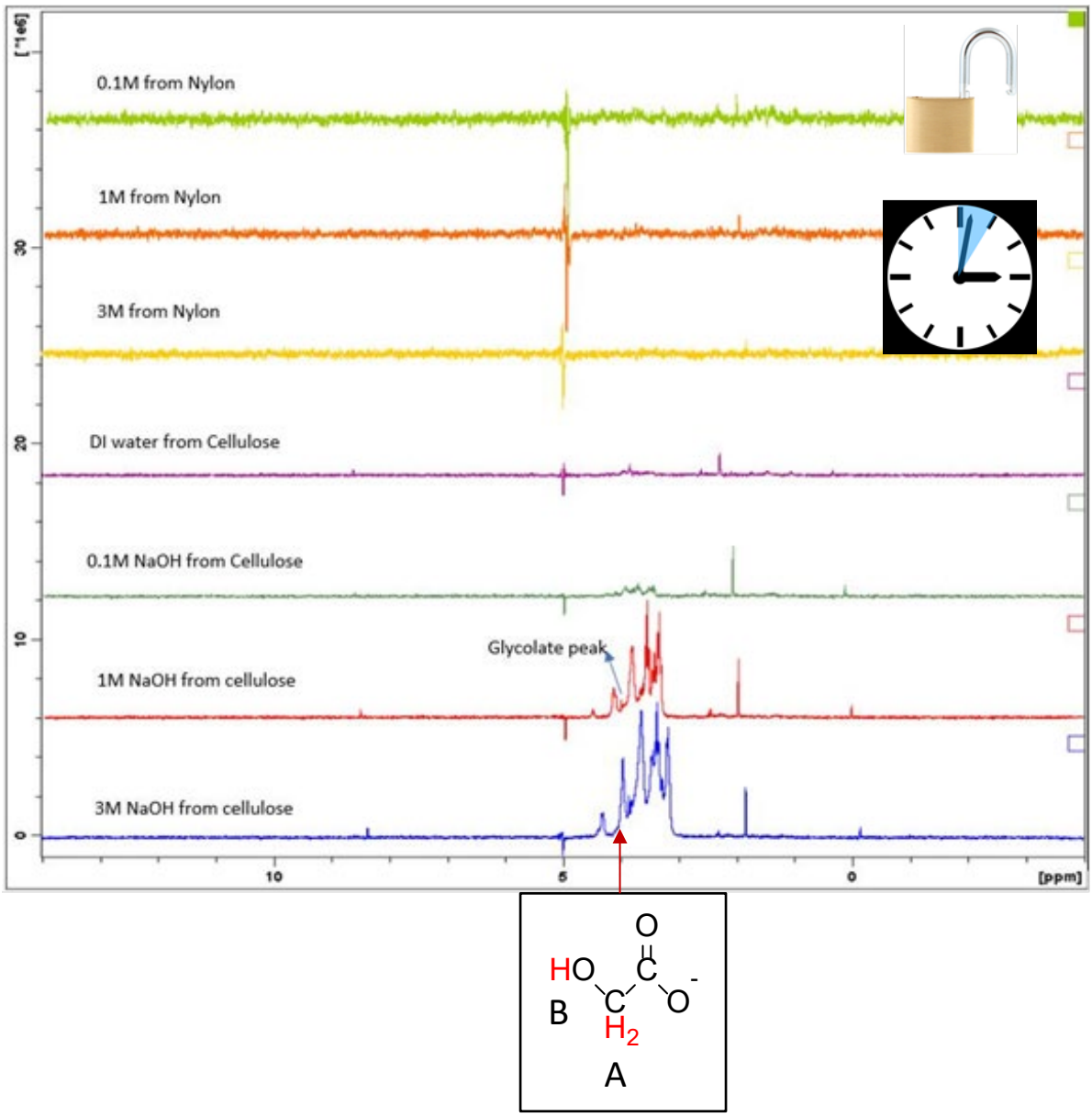

Figure 3-8 Filter Media Exposed to 0.1 M, 1.0 M, and 3.0 M NaOH Where Nylon is Baseline Resolved at 3.9 ppm Where Glycolate CH2 Response Appears

SRNL personnel analyzed decontaminated Tank 22 (HTF-22-20-69) samples containing 0, 5, 10, 25, and 50 mg/L of glycolate using unlocked H NMR. Figure 3-9 shows the overlapping spectrum of the CH_2 response (A). The S/N can be used to visually determine the LOD at S/N=3 (~5 mg/L) and the LOQ at S/N=10 (~10 mg/L).[25] Each response was scanned 32 times at 9 seconds a scan with a total analysis time including sample changeover of about an hour. The S/N increases as the square root of the number of scans $\sqrt{n}$; thus, many scans will be required to improve sensitivity.

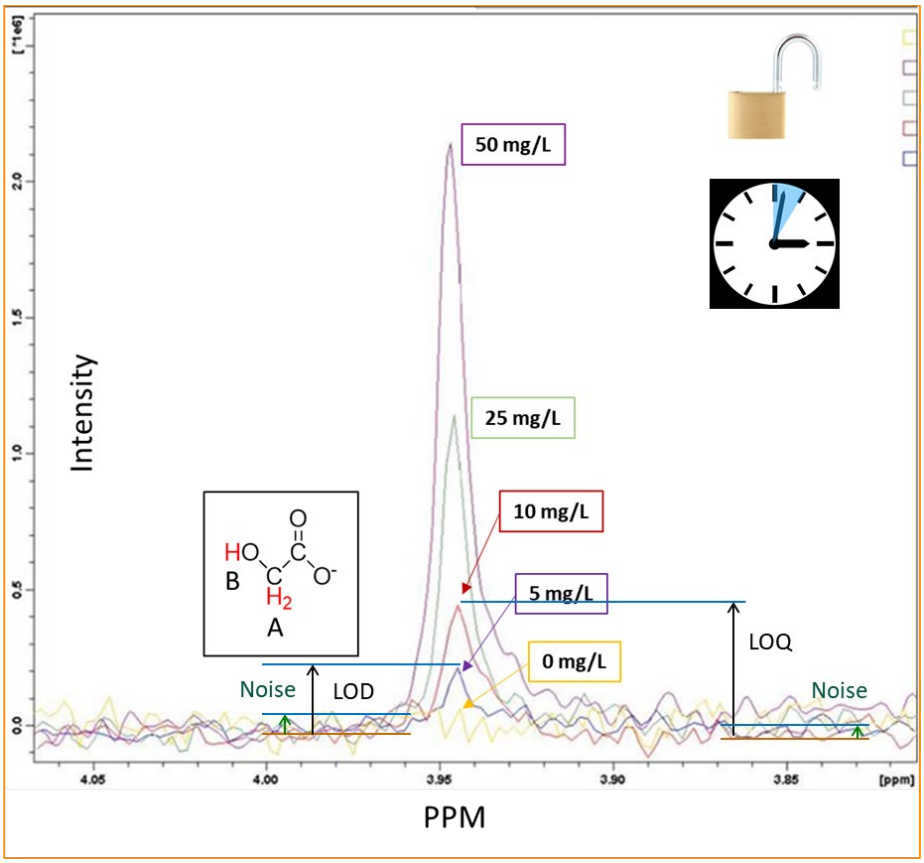

Figure 3-9: Multiple Tank 22 Samples with Increasing Concentrations of Glycolate (A) + (Scan = 32, 9 Seconds per Scan)

Figure 3-10 demonstrates the increase of sensitivity with increasing number of scans. The 5 mg/L Tank 22 spike sample was analyzed by increasing the number of scans which improved the S/N by $\sqrt{n}$.

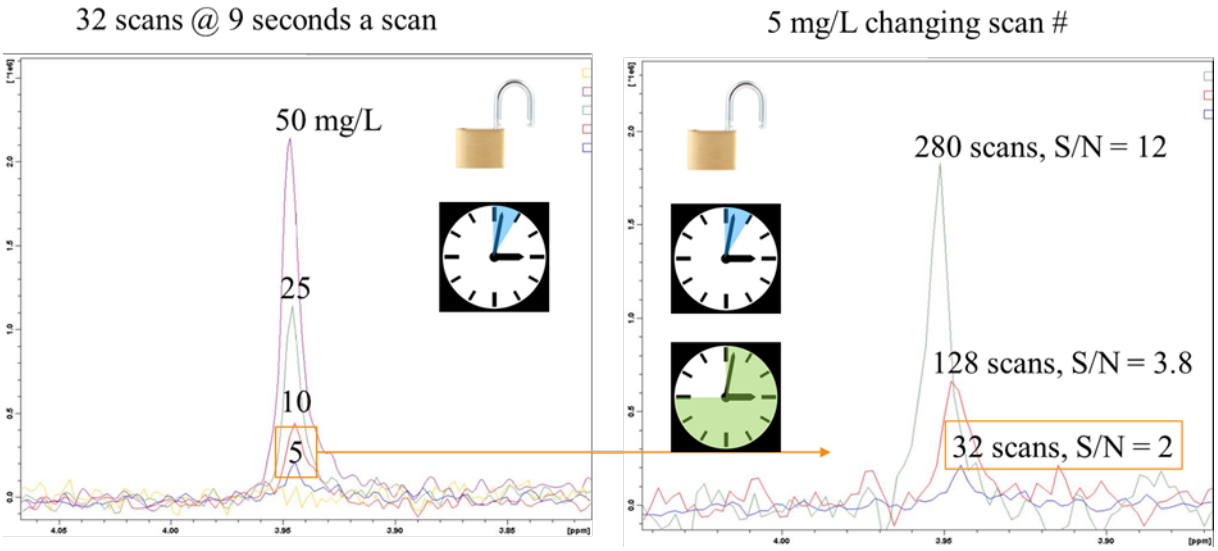

Figure 3-10: Multiple Tank 22 (HTF-22-20-69) Samples Where the 5 mg/L Glycolate Spike Increases S/N with More Scans

When the number of scans was increased to 128 (9 seconds per scan) on a large set of glycolate Tank 22 samples to improve sensitivity, the optimization of the stationary magnetic field homogeneity (H_0) drifted resulting in loss of resolution. In general, the magnet remains optimized or "shimmed" when unlocked for about an hour. Figure 3-11 demonstrates the loss of resolution and broadening of the NMR peaks. The standards analyzed later (5, 10, and one of the 25 mg/L) have broad peak shapes due to magnet drift. To prevent magnetic drift during long scan times, D_2O is added to each sample and used as a reference or to "lock on", keeping the magnetic field optimized.

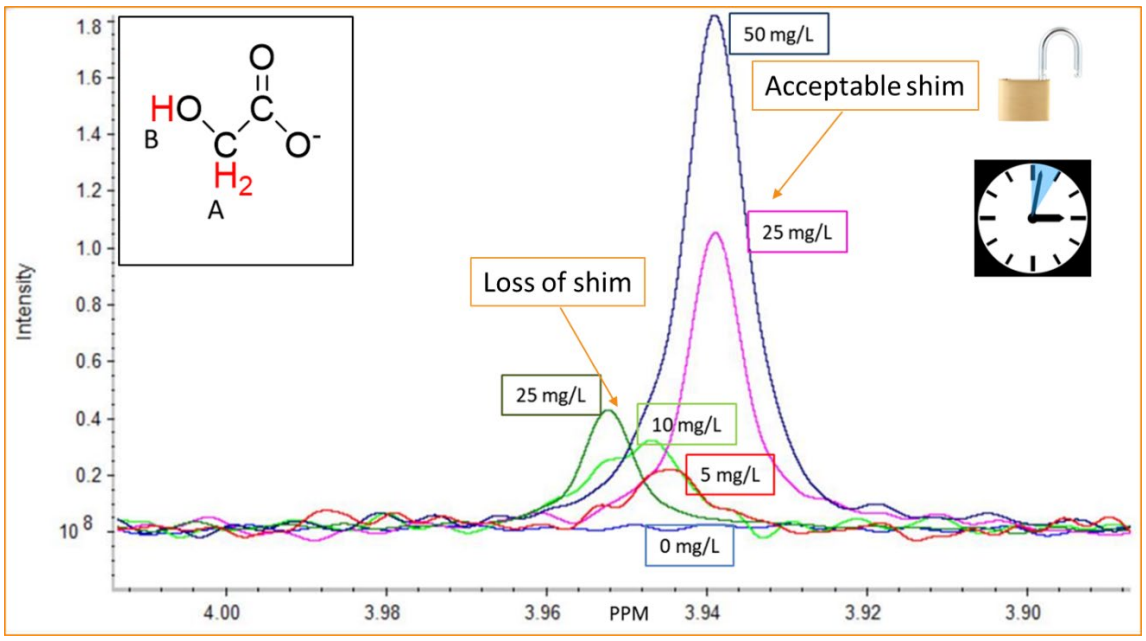

Figure 3-11 Multiple Tank 22 Samples with Increasing Concentrations of Glycolate (A) Where the 5, 10, and 25 mg/L Samples Broadened due to Applied Magnetic Field Drift or Loss of "Shim"

3.6 Adjusting pH of High Ionic Strength Samples to Lower Viscosity and Adding D_2O to Lock the Magnet

To achieve higher sensitivity on evaporator feed tanks, the sample preparation method was modified from Figure 1-2. The sample hydroxide concentration is lowered to below 0.1 M with nitric acid and a locking compound (D_2O) is added. The samples are then treated with ion exchange resin (CST/MST) multiple times and filtered through a 0.45-micron PES filter each strike. With the dose lowered, the samples are aliquoted into NMR tubes in a containment unit and sent for analysis. The cell blank ensures no interferences are observable at 3.9 ppm from sample preparation.

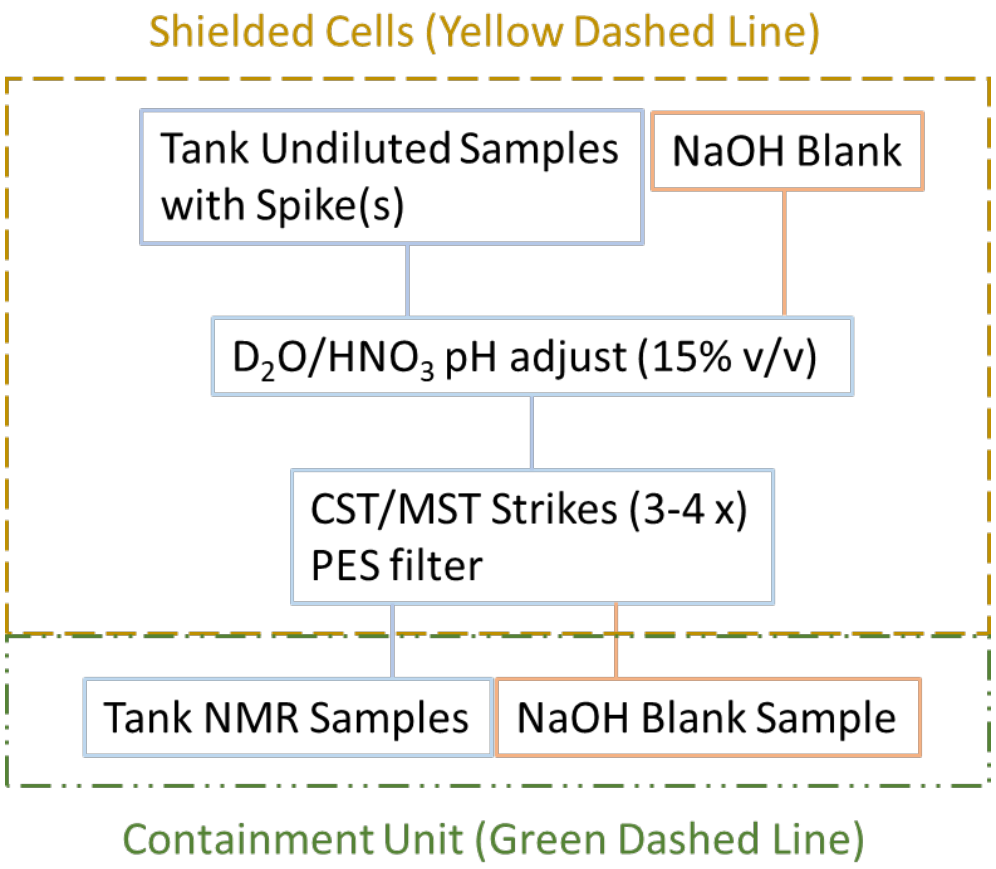

Figure 3-12 Schematic for High Ionic Strength Tank Sample Preparation for H NMR

SRNL personnel tested the Figure 3-12 sample preparation protocol using simulant containing known concentrations of glycolate and acetate. Acetate was added to each as an internal standard for the H NMR analyses and Table 3-1 summarizes the make-up of the solutions. IC of the sample determined 65 mg/L glycolate (expected 64 mg/L) and the chromatogram is shown in Figure 3-13. No loss of glycolate was observed from the sample preparation. Additionally, 30% of Na (ICPES) was removed from the simulant and a Cs removal factor of ~30,000 was observed using a Cs-137 spike and gamma counting.

Table 3-1: Simple Test Simulant for pH Adjustment PES Filter Protocol

Sample	1000 mg/L glycolate, mL	1000 mg/L acetate, mL	7 M NaOH, mL	8 M HNO_3, mL	H_2O, mL	V_t, mL	Final OH, M	Final spike conc. glycolate/ acetate, mg/L	Comment	IC results, mg/L
NaOH spikes	0.800	0.500	6.00	5.20	0.200	12.7	0.0315	64/40	PES, 4 CST/1 MST, 4 strikes	65
NaOH acetate	0	0.500	6.00	5.20	1.00	12.7	0.0315	0/40	PES, 4 CST/1 MST, 4 strikes	<50
NaOH	0	0	6.00	5.20	1.50	12.7	0.0315	0/0	PES, 4 CST/1 MST, 4 strikes	<50

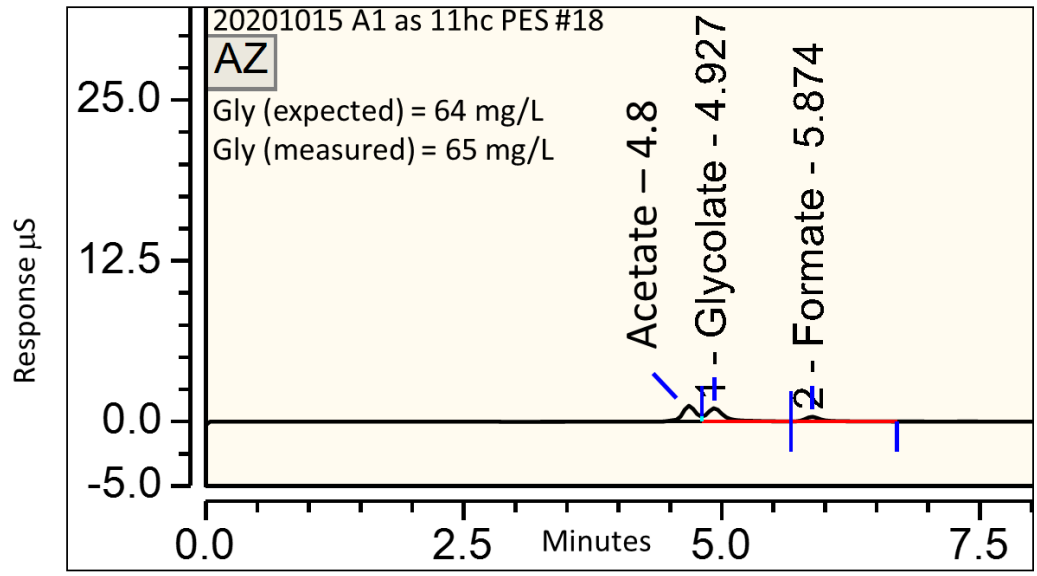

Figure 3-13: Analysis of Simple Hydroxide Simulant Containing 64 mg/L Glycolate and 40 mg/L Acetate After pH adjustment and Four Ion Exchange Strikes – no Loss of Glycolate

Additionally, H NMR responses from sample preparation impurities in the region of glycolate (3.9 ppm) were not present as seen in Figure 3-14. Acetate (1.9 ppm) and formate (8.3 ppm) consistently appear in the blank (labelled NaOH) and are impurities from high ionic strength sample processing. Benzilic acid (7.3 ppm) replaced acetate as an internal standard in later analyses.

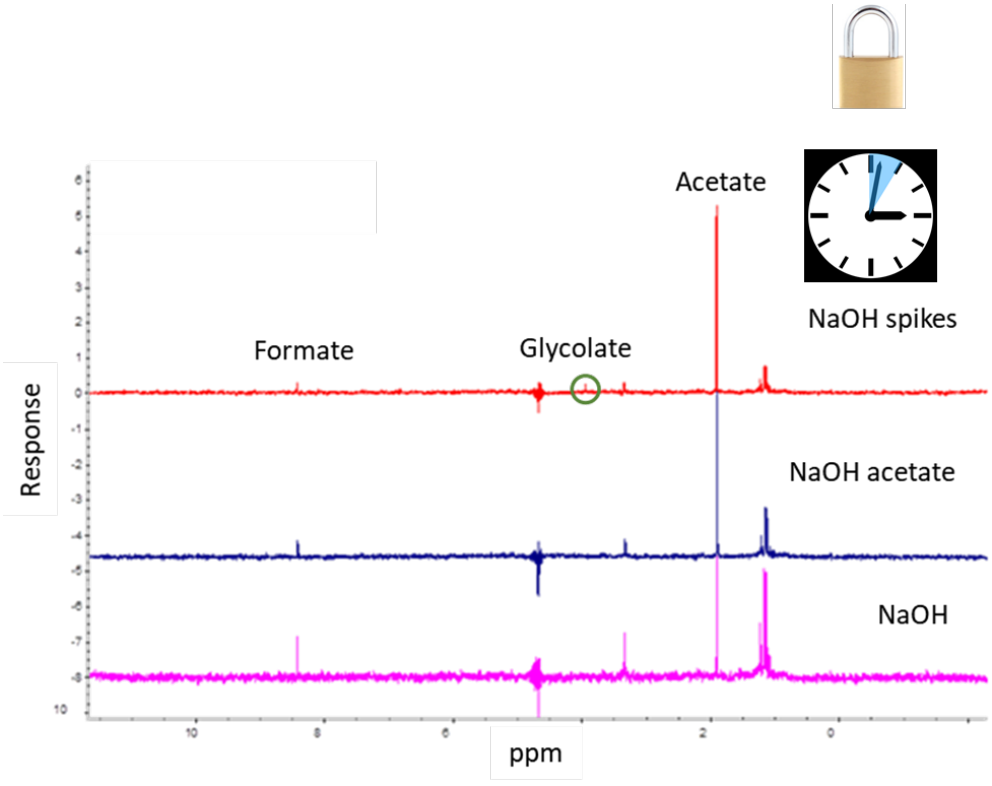

Figure 3-14: Simple Test Simulant (1.25 mL) with D_2O (0.25 mL) Analyzed by H NMR After pH Adjustment and Four Ion Exchange Strikes with PES Filtration as Shown in Figure 3-12

3.7 Tank 22 Glycolate Analysis no pH Adjustment

Tank 22 was analyzed unlocked by SAM to give an LOQ of 6 mg/L and an LOD of 2 mg/L with a linearity of R^2=0.9988. Appendix D contains the error analysis and LOD/LOQ calculation. This unlocked method was demonstrated in a previous report.[1]

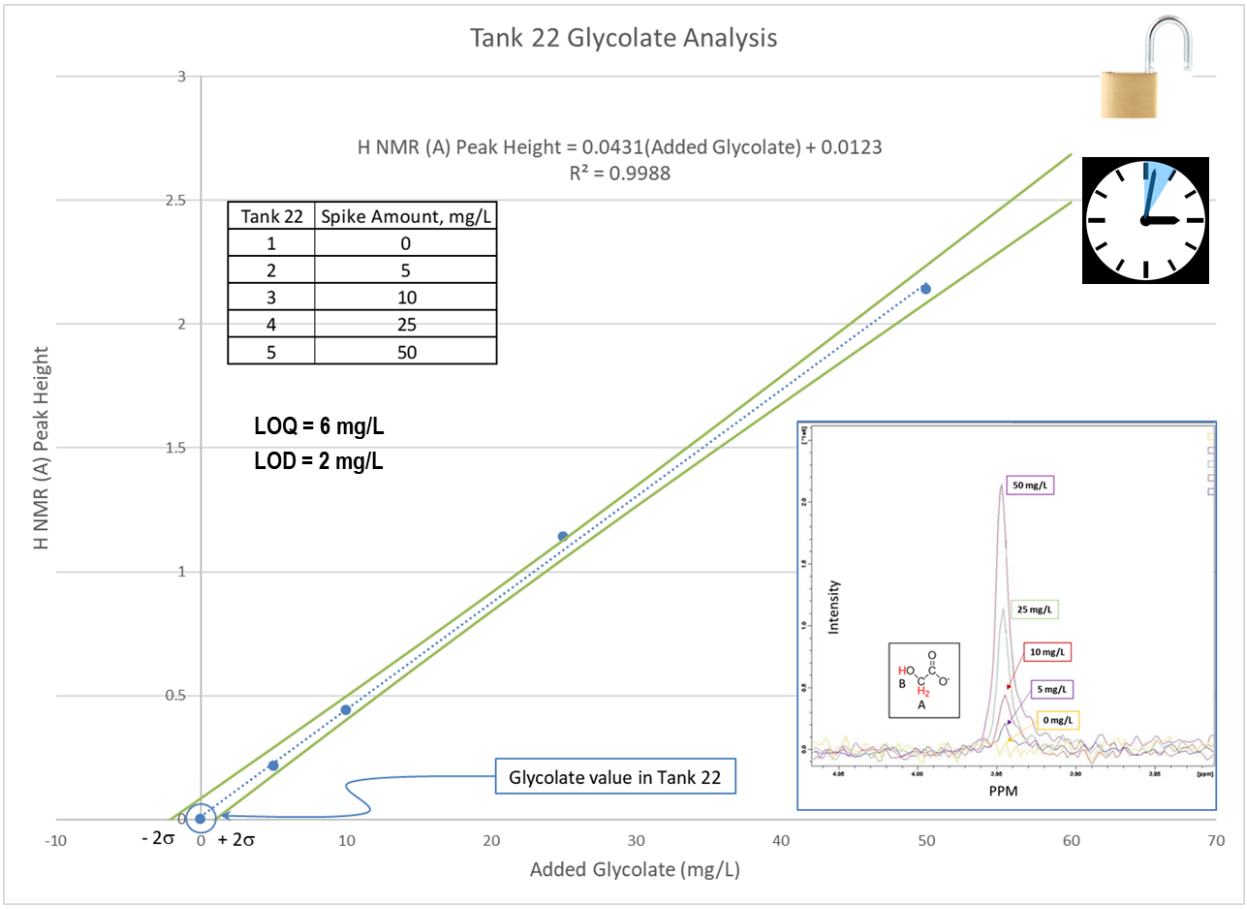

Figure 3-15: Standard Addition Method Unlocked H NMR Analysis (32 Scans, 9 s)

A second Tank 22 H sample was prepared as shown in Figure 3-16 where the locking agent D_2O was added slightly diluting the sample. Benzilic acid was used as an internal standard and the samples were filtered through a PES filter after each ion exchange strike.

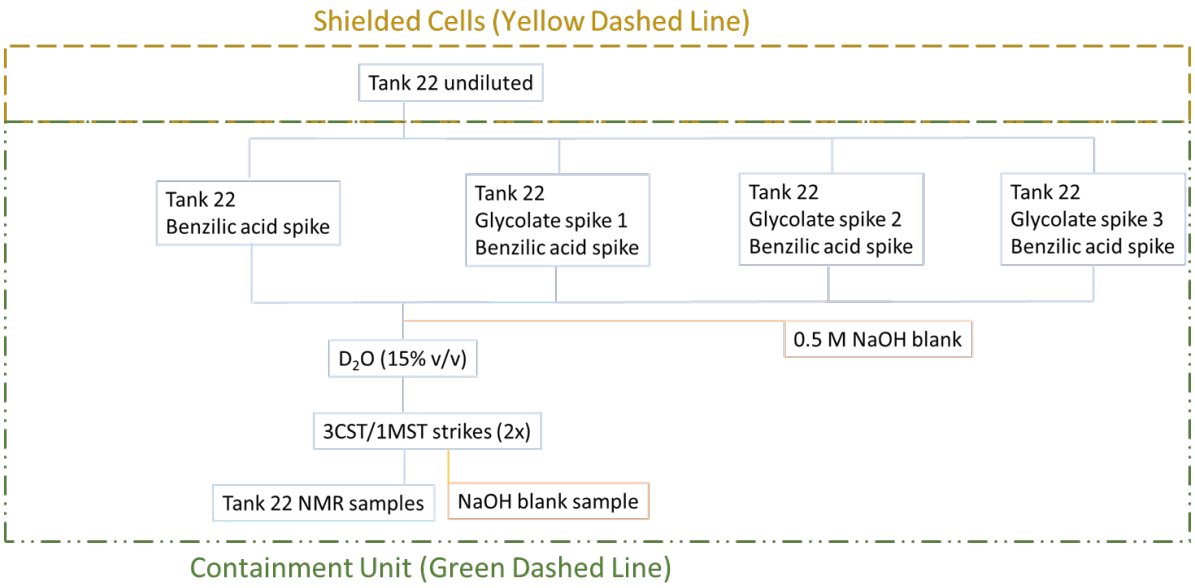

Figure 3-16: SAM in Tank 22 using Benzilic Acid as an Internal Standard

Like the previous sample, H NMR glycolate analysis showed linearity (R^2=0.9939 with an LOQ of 8 mg/L and LOD of 3 mg/L in the slightly diluted sample (Appendix D)). The LOQ and LOD results closely matched the unlocked H NMR analysis of Tank 22 since each of the number of scans was the same. With the addition of D_2O, the number scans can be increased from 32 to 256 per sample to reach an LOD of 1 mg/L.

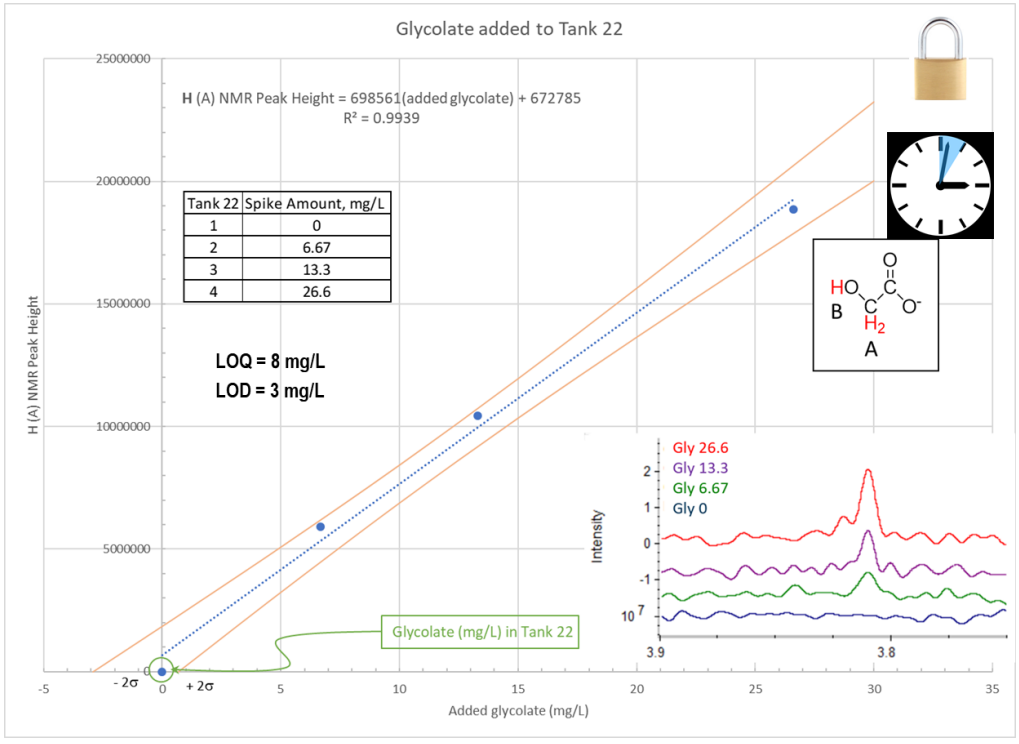

Figure 3-17: Tank 22 Locked SAM for Glycolate Analysis (32 Scans, 9 s)

3.8 Tank 37 Glycolate Analysis with pH Adjustment with Nitric Acid/D_2O

A high ionic strength Tank 37 LWS sample was used to develop the pH adjustment protocol. Figure 3-18 is read top to bottom where a sample is split and glycolate is spiked into one of the two samples. In this approach, acetate was added as an internal standard into both samples. In later work, acetate was replaced with benzilic acid because acetate was determined from the blank to be an impurity introduced into the sample during processing. The total base value of the sample is used to determine the volume of nitric acid in D_2O to be added to reach a total base value of <0.1 M. Personnel performed two ion exchange strikes in the Shielded Cells and two in a containment unit where the sample is filtered (PES) each time. Each sample is then put in an H NMR tube for analysis.

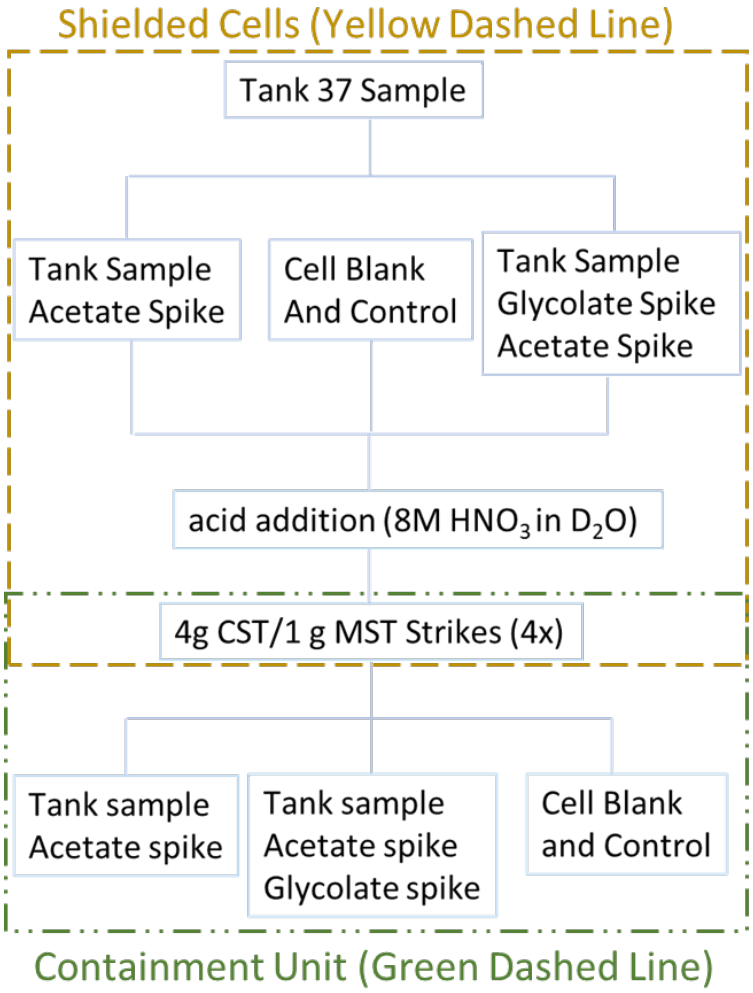

Figure 3-18: Tank 37 pH Adjustment Protocol

In Figure 3-19, the brown circle identifies where the Lorentzian glycolate peak falls in the four chromatograms shown. The spiked sample (1) shows a strong signal (S/N=43) while the sample without glycolate (2) shows a flat baseline. Acetate and formate are impurities found in the blank (3). The control (4) also shows a glycolate peak (S/N = 29). In Figure 3-20, the spiked sample (1) was scanned for a long period (4 h) and the peak height increased (S/N = 94) to give an estimated LOQ of 14 mg/L and LOD of 4 mg/L.

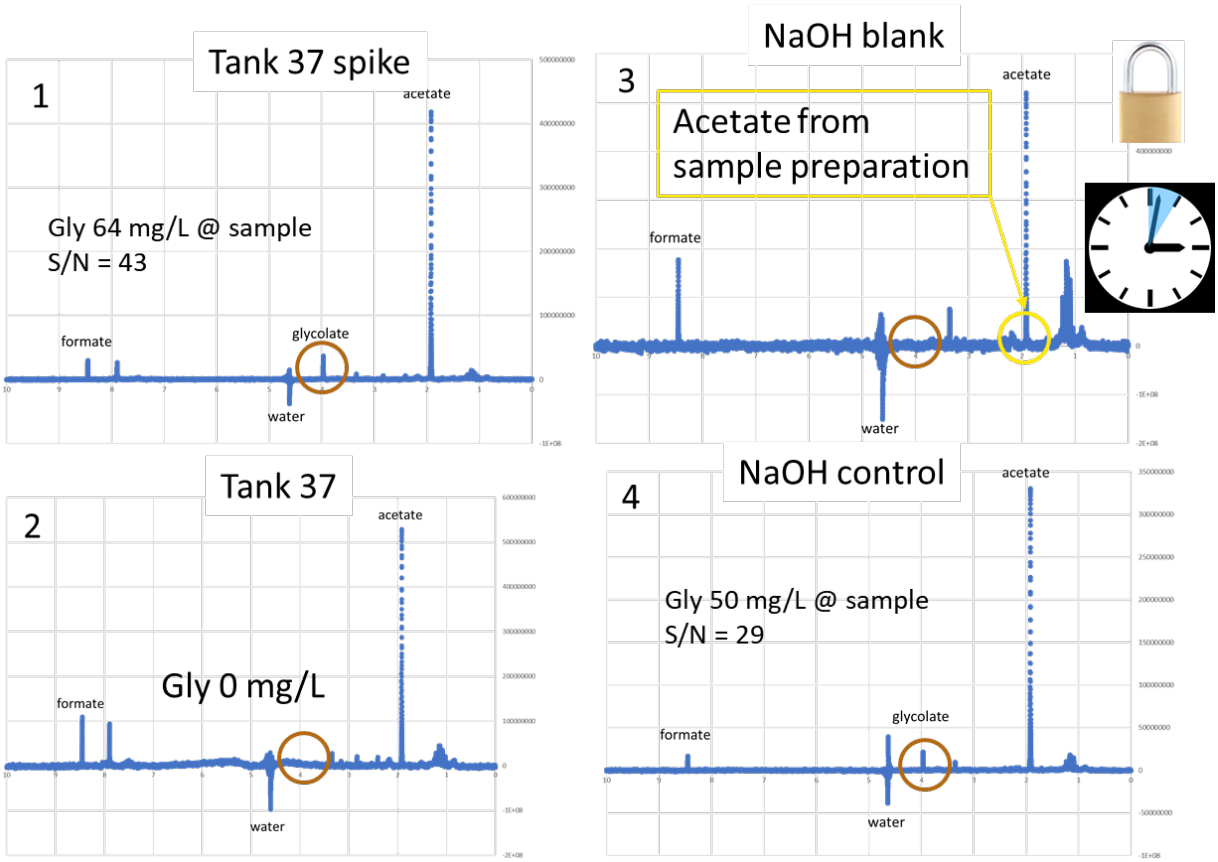

Figure 3-19: Tank 37 LWS sample analyzed by H NMR

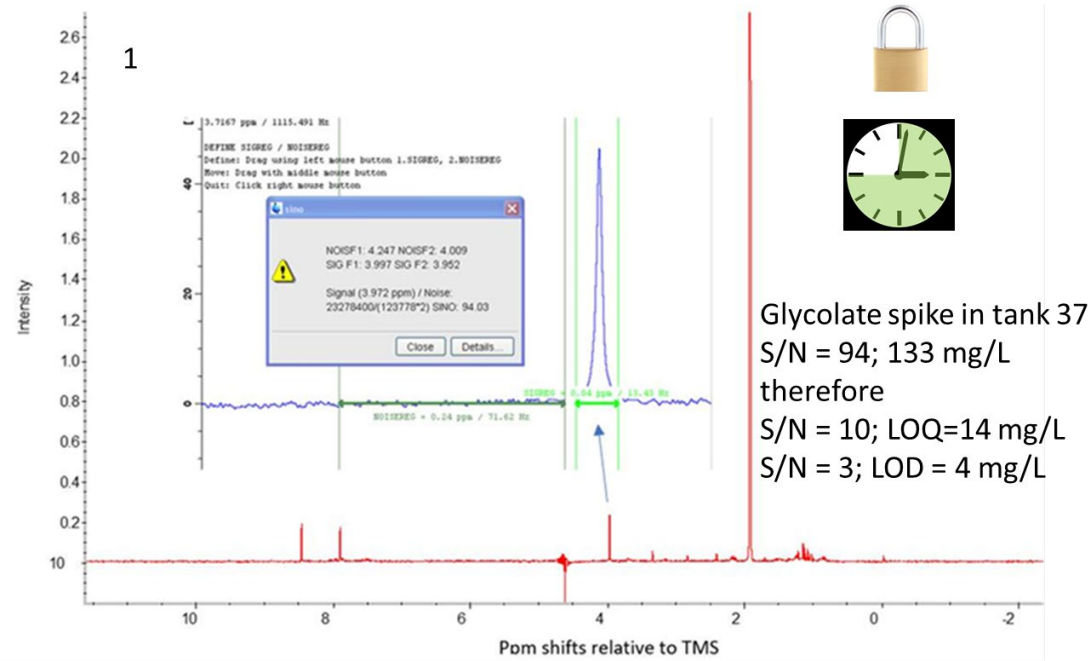

Figure 3-20: Tank 37 LWS sample (1) Analyzed Locked for a Long Period (4 h)

3.9 Tank 38 SAM Glycolate Analysis with pH Adjustment

A Tank 38 sample was split as shown in Figure 3-21. Spikes were added and the appropriate volume of nitric acid was added based on the total base of the sample to adjust the final concentration (Appendix D) to below 0.1 M. After ion exchange strikes, samples were loaded in H NMR tubes for analysis.

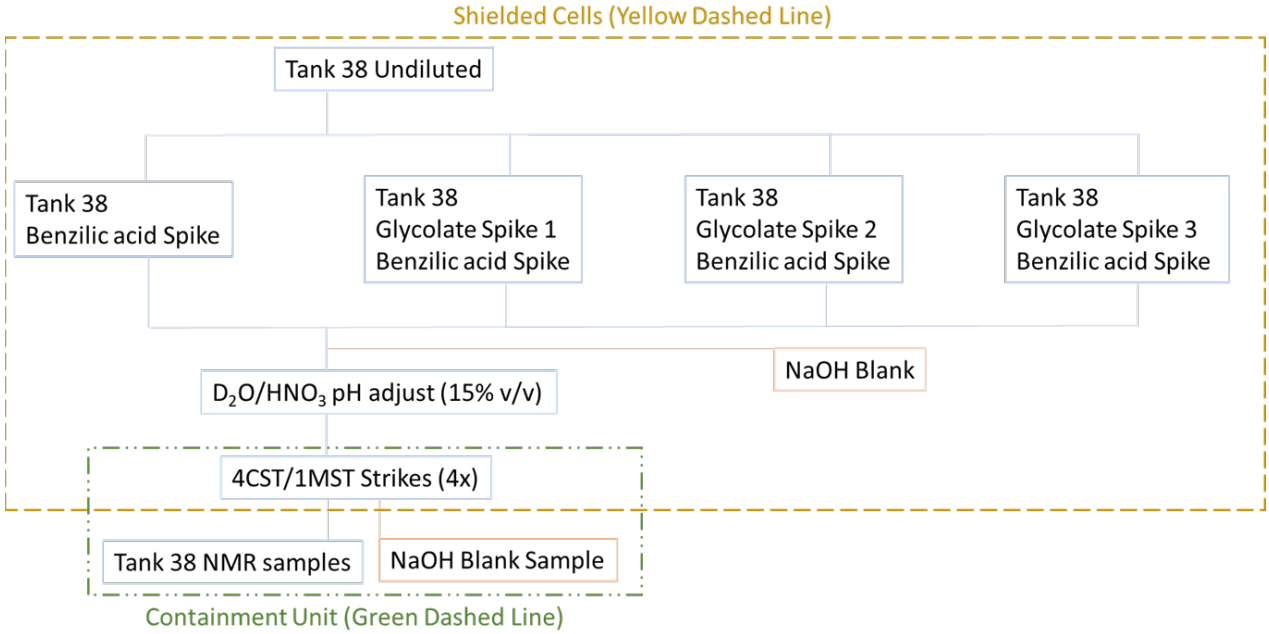

Figure 3-21: Tank 38 Sample Glycolate Analysis Protocol

The sample showed a minimal response at 1 mg/L (red) but an observable peak was present at 6.2 mg/L (dark blue) as shown in Figure 3-22.

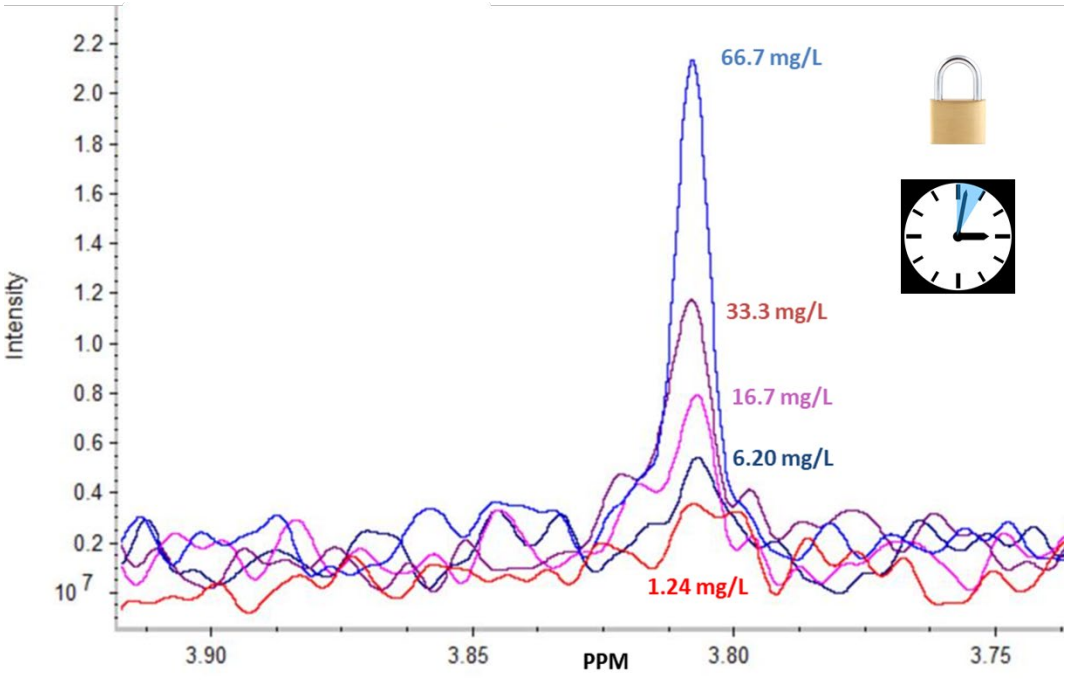

Figure 3-22: Multiple Tank 38 LWS Samples Spike with Increasing Concentration of Glycolate

SAM gave a straight line (R^2 = 0.9995) for the Tank 38 LWS sample as shown in Figure 3-23. The LOQ was 5 mg/L and the LOD = 1.5 mg/L (Appendix D).

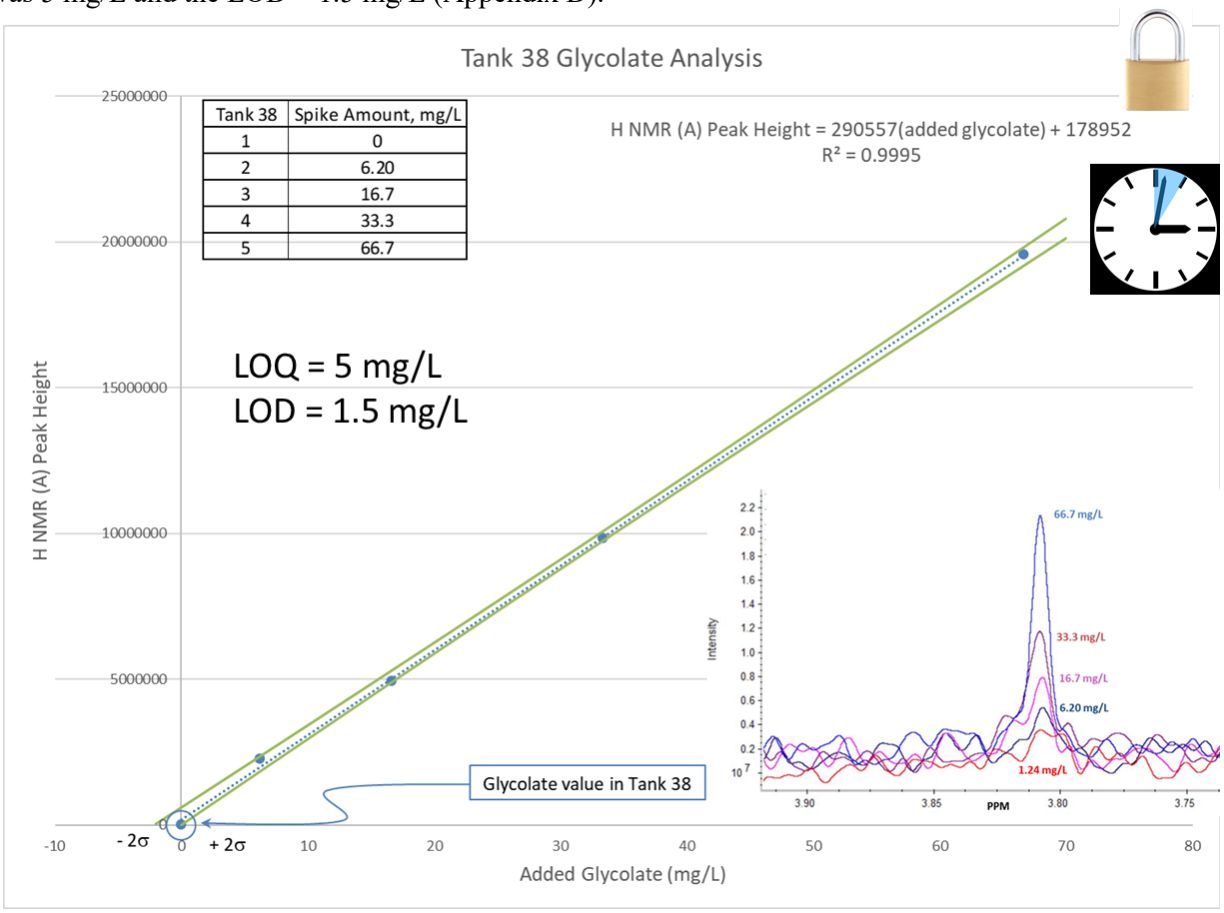

Figure 3-23: Tank 38 LWS sample SAM result

Increasing the number of scans lowered the LOD to <1 mg/L as shown in Figure 3-24.

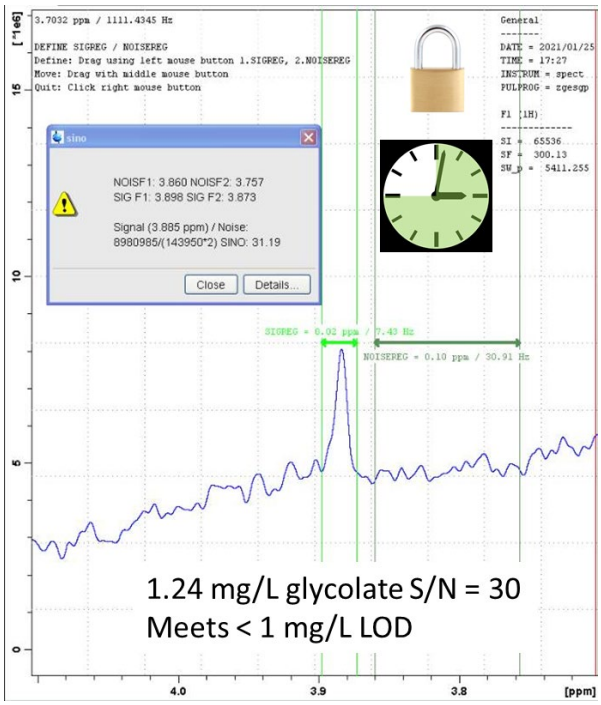

Figure 3-24: Tank 38 LWS Sample (Scans = 1800 @ 9 Seconds per Scan)

3.10 Tank LWS Sample Logistics

Figure 3-21 is a schematic of how future high ionic strength Tank LWS samples will be prepared for analysis. All materials for the analysis will be organized into kits. Each kit will be for one sample split and will contain the appropriate bottles, spikes, reagents, and filtration unit. The kits will be processed one by one through the cells to keep the multistep process organized and avoid errors. Tank samples will be processed through the cells and the tank sample initially will be analyzed without glycolate (internal standard only) and compared to a split sample with a 1 mg/L glycolate spike (plus internal standard). Tanks with no glycolate will be reported as <1 mg/L. If glycolate is present in the tank sample, spiked analysis or SAM may be used to quantitate.

4.0 Conclusions

This work extended the analytical capabilities for glycolate analysis in high ion strength LWS samples by developing and demonstrating innovative H NMR techniques and a novel sample preparation protocol involving pH adjustment, locking agent addition, and ion exchange decontamination protocol. The method allows the user to directly view glycolate in LWS samples with minimal dilution. When compared to IC, this method achieved lower LOQ and LOD values for high ionic strength samples. Additionally, the method may be used to directly view undiluted/slightly diluted tank waste to identify other-select organic compounds. This analytical protocol and analysis are time consuming and manually labor intensive when compared to IC. Thus, the most appropriate application of the H NMR method should target determining glycolate at concentration levels below 10 mg/L in tank waste.

5.0 Recommendations, Path Forward or Future Work

Improvements to sensitivity could be achieved using an NMR instrument with a larger magnet. An NMR instrument with a 600 MHz magnet will improve sensitivity 3 times that of the existing instrument. Additionally, an internal standard that can also perform as a lock, such as 3-(trimethylsilyl)propionic-2,2,3,3-d_4 acid sodium salt, may warrant evaluation.

6.0 References

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Appendix A. Scoping H NMR Simulant Samples Preparation Sheets: Metal Removal, Varying Molarity, Methanol Samples, and SAM Samples

Metal removal experiments (section 3.2)

R&D Directions **Reference: PS PL-AP-4006**

1. PI: Thomas White 2. Task Title: Analysis for NMR Glycolate Simulant Samples
3. Date: 9/7/2020 Customer Name: F Analyst: TLW
4. Work Group and Location: Analytical Development, Bldg. 773A, Lab B134
5. Applicable Reference Documents: L1 Manual, AD Procedure 2310 Analysis of Solutions by IC; HAS # SRNL-HA-01236

Method **NMR (glycolate)** 1000 mg/L 32540

- Calibration and QC Standards preparation:

_____ Record Lot# of Calibration Standards

218045098-01 Record Lot# of QC Standards

30664 31093 Record ID of Pipettes used

For H NMR, we will generate 3 samples:

6 M Na simulant spike 50 (2.0 mL) 25 mg/L EDTA ✓

6 M Na simulant spike 50 (2.0 mL) Biotage Silica Thiol ✓ + Blank (10 mL H2O 5 mL sample collect 2 mL at end)

6 M Na simulant spike 50 (20 mL) OnGuard II H+ ✓

Spikes (50 mg/L) in simulant samples

✓ Use 1000 mg/L standard

✓ Spikes:

Target Concentration / ID	Glycolate Bottle A (1000 mg/L), µL	6M Na Simulant, µL	Dilution	Glycolate Conentration, mg/L	Treatment
6M Na Simulant 50 mg/L	100	1900	20	50	25 mg/L EDTA
6M Na Simulant 50 mg/L	100	1900	20	50	Biotage Silica Thiol 60 mg
6M Na Simulant 50 mg/L	1000	19000	20	50	OnGuard II H+
6M Na Simulant 50 mg/L	0	20000	0	0	OnGuard II H+ blank

	MW	vol, mL	Wt, g std, mg/L		
EDTA dihydrate	372.2	10	0.01	1000	1380 mg/L
	336.21		0.0138		1242 mg/L EDTA

1242 X / 2000 = 2000 (25) ⇒ 40 mL

____ Save alquot for 3 mL for Fernando NMR tubes (no CST).

Fernando Fondeur

(spike amount) Glycolate in 6 M Na Simulant

Corrosive

Date

Varying the OH with 50 mg/L glycolate experiment (section 3.2)

R&D Directions **Reference: PS PL-AP-4006**

1. PI: Thomas White 2. Task Title: Analysis for IC Glycolate Simulant Samples
3. Date: 7/23/2020 Customer Name: F Fondeur Analyst: TLW
4. Work Group and Location: Analytical Development, Bldg. 773A, Lab B134
5. Applicable Reference Documents: L1 Manual, AD Procedure 2310 Analysis of Solutions by IC; HAS # SRNL-HA-01236

Method **NMR (glycolate)**

- Calibration and QC Standards preparation:

218045098-01 Record Lot# of Calibration Standards 32570 ; Balance 29710 ; WC

Record Lot# of QC Standards 10,000 g

31093 (1 mL) 30664 (10 mL) Record ID of Pipettes used

1.0020 g

For H NMR, we will generate 4 samples:

5 M Na simulant spike 50 (2.0 mL)

4 M Na simulant spike 50 (2.0 mL)

3 M Na simulant spike 50 (2.0 mL)

2 M Na simulant spike 50 (2.0 mL)

1 M Na simulant spike 50 (2.0 mL)

Spike (50 mg/L) in simulant samples of varying molarity

✓ Use 1000 mg/L standard

✓ Spikes:

Target Concentration / ID	Glycolate Bottle A (1000 mg/L), µL	6M Na Simulant, µL	H2O, µL	Total Volume, µL	Glycolate Conentration, mg/L
5M Na Simulant 50 mg/L	100	1615	285	2000	50
4M Na Simulant 50 mg/L	100	1290	610	2000	50
3M Na Simulant 50 mg/L	100	970	930	2000	50
2M Na Simulant 50 mg/L	100	645	1255	2000	50
1M Na Simulant 50 mg/L	100	325	1575	2000	50

✓ Send for Fernando NMR tubes (no CST).

Fernando Fondeur

(spike amount) Glycolate in 6 M Na Simulant

Corrosive

Date

Glycolate SAM in 6M Na simulant (only 50 mg/L peak was observable) (section 3.2)

R&D Directions **Reference: PS PL-AP-4006**

1. PI: Thomas White 2. Task Title: Analysis for IC Glycolate Simulant Samples
3. Date: 7/6/2020 Customer Name: #3 Analyst: TLW
4. Work Group and Location: Analytical Development, Bldg. 773A, Lab B134
5. Applicable Reference Documents: L1 Manual, AD Procedure 2310 Analysis of Solutions by IC; HAS # SRNL-HA-01236

MTE # 29710

Method **Anions (glycolate)**

Instrument (select one) ***(SYSTEM 1)*** ***(SYSTEM 2)*** 29710

- Calibration and QC Standards preparation:

9.9998 g

218045098-6 Record Lot# of Calibration Standards

Record Lot# of QC Standards 100.0045

B605067758 (1mL) 30664 (10mL) Record ID of Pipettes used

For H NMR, we will generate 4 samples: 10.0282 g 1.00135

6 M Na simulant no spike (20 mL)

6 M Na simulant spike 10 (20 mL)

6 M Na simulant spike 25 (20 mL)

6 M Na simulant spike 50 (20 mL)

Spikes (10, 25, and 50 mg/L) in simulant samples

____ Use 1000 mg/L standard

____ Spikes:

Target Concentration / ID	Glycolate Bottle A (1000 mg/L), µL	6M Na Simulant, µL	Dilution	Glycolate Conentration, mg/L	# of vials
6M Na Simulant		20000 25.49 g	0	0	1
6M Na Simulant 50 mg/L	1000 ~~0.9886~~	19000 24.19 g	20	50	1
6M Na Simulant 25 mg/L	500 0.4878	19500 24.81 g	40	25	1
6M Na Simulant 10 mg/L	200 0.1968	19800 25.22 g	100	10	1

total wt
36.93
36.66
36.84
38.91

____ Save alquot for 3 mL for Fernando NMR tubes (no CST).

Fernando Fondeur

(spike amount) Glycolate in 6 M Na Simulant

Corrosive

Date

____ Send four simulant samples to David DiPrete with labels.

David DiPrete

(spike amount) Glycolate in 6 M Na Simulant

Corrosive

Date

Appendix B. Scoping H NMR Simulant Methanol Samples SAM

Methanol SAM experiment no D2O, pH adjustment, or ion exchange titanates (16 scans @ 12 seconds a scan - excellent peak heights)(results in section 3.3)

R&D Directions **Reference: PS PL-AP-4006**

1. PI: Thomas White 2. Task Title: Analysis for IC Glycolate Simulant Samples
3. Date: 10Jul20 Customer Name: Fondeur, F. Analyst: L. Cheatham
4. Work Group and Location: Analytical Development, Bldg. 773A, Lab B134
5. Applicable Reference Documents: L1 Manual, AD Procedure 2310 Analysis of Solutions by IC; HAS # SRNL-HA-01236

Method **NMR (methanol)**

For H NMR, we will generate 4 samples:

6 M Na simulant no spike (2 mL)

6 M Na simulant spike 10 (2 mL)

6 M Na simulant spike 25 (2 mL)

6 M Na simulant spike 50 (2 mL)

Spikes (10, 25, and 50 mg/L) in simulant samples

✓ Use 1000 mg/L standard

✓ Put 12.6 µL (10 mg) methanol in 10 mL of water. (1000 mg/L; $d_{methanol}$ = 0.791 g/mL)

✓ Spikes:

Target Concentration / ID	Methanol (1000 mg/L), µL	6M Na Simulant, µL	Dilution	Methanol Conentration, mg/L	# of vials
6M Na Simulant		2000	0	0	1
6M Na Simulant 50 mg/L	100	1900	20	50	1
6M Na Simulant 25 mg/L	50	1950	40	25	1
6M Na Simulant 10 mg/L	20	1980	100	10	1

✓ 2 mL for Fernando NMR tubes.

Fernando Fondeur

(spike amount) Methanol in 6 M Na Simulant

Corrosive

Date 10Jul20

Methanol SAM experiment error analysis

		standard addition methanol								
		mg/L								
		spike	HNMR Height							
		0	0							
		10	1.10E+06							
		25	3.00E+06							
		50	5.70E+06							
	average	21.25								
	devsq	1418.75								
2 sigma error bars on regression (note that only measured points were included!)							Defined values			
Y = 114714 (X) + 12335							Slope, m	m	114714	
assumed x	calculated y	2 sigma	Calc y + 2 sigma	Calc y - 2 sigma			intercept,	b	12335	
-1.486	-158130.004	158136.1332	6.129157077	-316266.1372	y-intercept		Observati	n	4	
-0.1075	3.245	152522.6011	152525.8461	-152519.3561						
1.1775	147410.735	147430.427	294841.162	-19.69198531			Se	SYX	100877	
0	12335	152091.1979	164426.1979	-139756.1979			Average X	XAVG	21.25	
10	1159475	117504.5241	1276979.524	1041970.476			SSX	SSX	1418.75	
20	2306615	101098.9519	2407713.952	2205516.048				t	2	
30	3453755	111233.0308	3564988.031	3342521.969						
40	4600895	142347.042	4743242.042	4458547.958				=t*SYX*SQRT(1/n+(N7-XAVG)^2/SSX)		
50	5748035	184094.209	5932129.209	5563940.791				=(m*N7+b)+P7		
60	6895175	230774.304	7125949.304	6664400.696				=(m*N7+b)-P7		

Methanol SAM experiment linear regression LOQ and LOD calculation

			X	Y									
			calculated										
		measured	linear regressiobn										
		peak height	instrument				peform regression of instrument response in mg/L (x) to actual mg/L (y)						
		(counts)	response	actual			see associated spreadsheet for results						
			(mg/L)	(mg/L)			the LOQ = 10 x (Std error on intercept / slope)						
		0	-0.10753	0			the LOD = 3.3 x (Std error on intercept / slope)						
		1.10E+06	9.48154	10									
		3.00E+06	26.0445	25			**LOQ**		**LOD**				
		5.70E+06	49.5813	50			**6.63**		**2.19**				
	used to calculate column E												
	slope	114714											
	intercept	12335											
Line for methanol		Y = 114714 (X) + 12335											

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.999455378
R Square	0.998911053
Adjusted R Square	0.998366579
Standard Error	0.878903812
Observations	4

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	1417.205056	1417.205	1834.636	0.000544622
Residual	2	1.54494382	0.772472		
Total	3	1418.75			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	0.023141854	0.662354936	0.034939	0.975302	-2.826741421	2.873025129	-2.826741421	2.873025129
X Variable 1	0.998914045	0.02332132	42.83266	0.000545	0.898570505	1.099257584	0.898570505	1.099257584

RESIDUAL OUTPUT

Observation	*Predicted Y*	*Residuals*
1	-0.08426966	0.084269663
2	9.494382022	0.505617978
3	26.03932584	-1.039325843
4	49.5505618	0.449438202

Appendix C: Ion Exchange Strikes on Tank Waste

Tank	Identifier	Matrix	pH adjusted	Initial dpm/mL	Post Cells dpm/mL	Post Radiochemistry Lab, Final dpm/mL	Overall CSR decontamination factor	Comments
22 (average n=5)	HTF-22-20-91	Caustic Supernate	No	1.08E+08	n/a	1.28E+02	8.46E+05	<0.5 M total base, 2x 3g CST/1g MST 10 second contact in Radiochemistry
30 (average n=2)	HTF-30-20-32	Caustic Supernate	No	3.99E+09	2.10E+08	1.18E+07	5.07E+02	In Shielded Cells, 2x 4g CST/1g MST 30 seconds contact, in Radiochemistry 2x 4g CST/1g MST 10 second contacts
32 (average n=2)	HTF-32-20-29	Caustic Supernate	No	2.63E+09	3.12E+08	3.16E+07	1.06E+02	In Shielded Cells, 2x 4g CST/1g MST 30 seconds contact, in Radiochemistry 2x 4g CST/1g MST 10 second contacts
37 (average n=2)	HTF-37-20-25	Caustic Supernate	No	2.56E+09	1.91E+08	1.99E+07	1.74E+02	In Shielded Cells, 2x 4g CST/1g MST 30 seconds contact, in Radiochemistry 2x 4g CST/1g MST 10 second contacts
37 (average n=2)	HTF-37-20-26	Caustic Supernate	No	2.58E+09	1.96E+07	7.91E+05	4.38E+03	In Shielded Cells, 2x 4g CST/1g MST 30 seconds contact, in Radiochemistry 2x 4g CST/1g MST 10 second contacts
37 (average n=2)	HTF-37-20-90	Caustic Supernate	Yes	1.40E+09	7.79E+07	4.84E+04	4.95E+04	pH Adjusted, In Shielded Cells, 2x 4g CST/1g MST 1minute contact, in Radiochemistry 2x 4g CST/1g MST 30 second contacts
38 (average n=2)	HTF-38-20-62	Caustic Supernate	No	1.65E+08	3.07E+05	1.80E+04	3.15E+04	In Shielded Cells, 2x 4g CST/1g MST 30 seconds contact, in Radiochemistry 2x 4g CST/1g MST 10 second contacts
38 (average n=5)	HTF-38-20-103, 104	Caustic Supernate	Yes	2.16E+08	6.41E+02	2.35E+01	9.22E+06	pH Adjusted, In Shielded Cells - 2x 4g CST/1g MST 2 Minutes contact, in Radiochemistry - 2x 4g CST/1g MST 10 second contacts

Appendix D: Real Waste Testing Using Standard Addition Method (SAM)

Tank 22 HTF-22-20-69 unlocked SAM experiment no D2O or pH adjustment – Ion exchange titanates details in Appendix B (16 scans @ 9 seconds a scan)(results in section 3.7)

R&D Directions **Reference: PS PL-AP-4006**

1. PI: Thomas White 2. Task Title: Analysis for IC Glycolate Tank 22 spikes
3. Date: 8/19/2020 Customer Name: TLW/FS Analyst: TLW
4. Work Group and Location: Analytical Development, Bldg. 773A, Lab B134
5. Applicable Reference Documents: L1 Manual, AD Procedure 2310 Analysis of Solutions by IC

Method **Anions (glycolate)**

Instrument (select one) ***(SYSTEM 1)*** ***(SYSTEM 2)***

- Calibration and QC Standards preparation:

218045098-01 Record Lot# of Calibration Standards

_____ Record Lot# of QC Standards

_____ Record ID of Pipettes used 30664) 10 mL
31093 1mL

For H NMR, we will generate 7 samples:

0.6 M NaOH with 25 mg/L glycolate

Tank 22 no spike (2 mL)

Tank 22 spike 5 (2 mL) and water spike 5 (2 mL)

Tank 22 spike 10 (2 mL)

Tank 22 spike 25 (2 mL)

Tank 22 spike 50 (2 mL)

Spikes (0, 5, 10, 25, and 50 mg/L) in sample

✓ Spikes:

Target Concentration / ID	* Eluent (DI WATER)	Glycolate Bottle A (1000 mg/L)	Glycolate (200 mg/L)	Glycolate (100 mg/L)	Tank 22	# of vials
1000 mg/L standard	N/A	2000	N/A	N/A	N/A	1
200 mg/L standard	4000	1000	N/A	N/A	N/A	1
100 mg/L standard	4500	500	N/A	N/A	N/A	1
Tank 22	N/A	N/A	N/A	N/A	2000	1
Tank 22 50 mg/L	N/A	100	N/A	N/A	1900	1
Tank 22 25 mg/L	N/A	N/A	250	N/A	1750	1
Tank 22 10 mg/L	N/A	N/A	100	N/A	1900	1
Tank 22 5 mg/L	N/A	N/A	N/A	100	1900	1
Water Standard 5 mg/L	1900	N/A	N/A	100	N/A	1

Also have *control* (0.6 M NaOH with 25 mg/L glycolate), *water standard*, and spike (25 mg/L in Tank 22)

All but *control and water standard* went through CST procedure

✓ Send to Fernando

Tank 22 HTF-22-20-69 Error analysis

		HTF-22-20-69											
		16 scans	9 seconds										
		Example of standard addition				Hnmr peak height = M (glycolate added) + b							
		mg/L				M	b						
		spike	HNMR Height										
		0	0			0.042808184	0.020958						
		5	0.21357			0.042808184							
		10	0.442										
		25	1.141			r2							
		50	2.14			0.999232667							
	average	22.5											
	devsq	1225											
					slope	0.042808184	0.020958	Y-intercept					
					Uncertainty Slope	0.001186503	0.033821	Uncertainty on Y-intercept					
		2 sigma error bars on regression (note that only measured points were included!)							Defined values				
		Y =0.04280(X) +0.0209							Slope, m	m	0.0428		
		assumed x	calculated y	2 sigma	Calc y + 2 sigma	Calc y - 2 sigma			intercept, b	b	0.0209		
		-5	-0.1931	0.07509	-0.118011361	-0.268188639			Observations, n	n	5		
	estimated	0	0.0209	0.06504	0.085942198	-0.044142198			Se	SYX	0.041528		
		5	0.2349	0.05572	0.290615659	0.179184341			Average X	XAVG	22.5		
		10	0.4489	0.04753	0.496434671	0.401365329			SSX	SSX	1225		
		15	0.6629	0.04119	0.704087601	0.621712399	y-intercept			t	2		
		20	0.8769	0.03761	0.914514561	0.839285439							
		25	1.0909	0.03761	1.128514561	1.053285439				=t*SYX*SQRT(1/n+(N7-XAVG)^2/SSX)			
		30	1.3049	0.04119	1.346087601	1.263712399				=(m*N7+b)+P7			
		35	1.5189	0.04753	1.566434671	1.471365329				=(m*N7+b)-P7			
		40	1.7329	0.05572	1.788615659	1.677184341							
		45	1.9469	0.06504	2.011942198	1.881857802							
		50	2.1609	0.07509	2.235988639	2.085811361							
		55	2.3749	0.0856	2.460501887	2.289298113							
		60	2.5889	0.09643	2.685329382	2.492470618							

Tank 22 HTF-22-20-69 Linear regression for LOD/LOQ

		X	Y								
		calculated									
	measured	linear regressiobn									
	peak height	instrument			peform regression of instrument response in mg/L (x) to actual mg/L (y)						
	(counts)	response	actual		see associated spreadsheet for results						
		(mg/L)	(mg/L)		the LOQ = 10 x (Std error on intercept / slope)						
	0	-0.48832	0		the LOD = 3.3 x (Std error on intercept / slope)						
	2.14E-01	4.50164	5								
	4.42E-01	9.83879	10		**LOQ**		**LOD**				
	1.14E+00	26.1706	25		**5.16**		**1.70**				
	2.14E+00	49.5117	50								
used to calculate column E											
slope	0.0428										
intercept	0.0209										
	Y =0.04280(X) +0.0209										

SUMMARY OUTPUT

Regression Statistics	
Multiple F	0.999385686
R Square	0.99877175
Adjusted I	0.998362333
Standard E	0.816914441
Observati	5

ANOVA

	df	*SS*	*MS*	*F*	*gnificance F*
Regressio	1	1627.997952	1627.998	2439.499	1.83E-05
Residual	3	2.002047612	0.667349		
Total	4	1630			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*ower 95.0%*	*pper 95.0%*
Intercept	0.214700098	0.512966389	0.418546	0.703706	-1.41779	1.847188	-1.41779	1.847188
X Variable	0.993211027	0.020109033	49.39129	1.83E-05	0.929215	1.057207	0.929215	1.057207

RESIDUAL OUTPUT

)bservatio	*Predicted Y*	*Residuals*
1	-0.27030248	0.270302483
2	4.685774128	0.314225872
3	9.986689895	0.013310105
4	26.20758961	-1.207589607
5	49.39024885	0.609751148

Tank 22 HTF-22-20-91 locked SAM experiment no pH adjustment, D2O added, benzilic acid internal standard added, and ion exchange titanates added – details in Appendix B (32 scans @ 9 seconds a scan)(section 3.7)

R&D Directions

1. PI: ___David DiPrete IE0701-00394-30
2. Date: ____8-17-2020 B154/158
3. Task Title: ____CSR Gamma GMR/AHJ 12/14/20
4. Work Group and Location: ____Analytical Development 773-A B-Wing
5. Applicable Reference Documents (if any):
   - HAP, AHA, or JHA: _____ HAP gamma, __JHA #4 Filtering with Nalgene units on Manifold, #5 Filtering with self-contained Nalgene Units, #6 Gamma Counter Use, #7 Gamma Prep, #8 Hot Plate Use, #14 Nalgene Splash guard, #15 Oven Use, #17 Pipetting, #23 Syringe Filtering
   - Procedures (e.g., site, L1 or section specific):_____ L1, L16.1 ADS-2420 Gamma Sample Preparation and Analysis
   - Others:
6. Hazards (List unique activity-specific hazards):
   __See appropriate JHA's in Laboratory JHA binder for identified hazards that can be encountered in sample preparation and analyses
7. Hazard Controls (List activity-specific hazard controls for above hazards):
   ___See appropriate JHA's for steps to mitigate identified hazards
   Work Zones may be expanded beyond 5 feet to space on adjacent countertops if needed
   When using scissors for cutting operations such as trimming Kimpack surface protector, cutting open sample bags, cutting tape to manageable lengths, etc… in the radiological material radiobench or radiohood containment units, maintain a visible separation between the point being contacted with scissors and the hand supporting the item being cut. If a visible separation cannot be maintained, wear a cut-resistant glove (leather or Kevlar) on the hand supporting the item being cut.
8. **Directions**

CSR Gamma Prep for Tom White's Tank 22 Glycolate run with Heavy Water, Benzilic Acid and Glycolate

(Wear your nitrile gloves)

Charge 02PUL4W543 for 15 hours (Two People)
CSR Gamma

Ale. Can you weigh out D2O from B-003, Record Balance used 30354

15ml Bottle labeled Tk22B20, Pipette 1.2ml D2O into bottle, weigh, record weight 1.309g

15ml Bottle labeled tk22B20G20, Pipette 1.2ml D2O into bottle, weigh, record weight 1.310g

15ml Bottle labeled tk22B20G10, Pipette 1.2ml D2O into bottle, weigh, record weight 1.321g

DPD

15ml Bottle labeled tk22B20G5, Pipette 1.2ml D2O into bottle, weigh, record weight 1.328g

15ml Bottle labeled tk22CSR1216, Pipette 1.2ml D2O into bottle, weigh, record weight 1.329g and 1.305g

15ml Bottle labeled CTRLtk221216, Pipette 1.2ml D2O into bottle, weigh, record weight 1.325g

15ml Bottle labeled BLKtk221216, Pipette 1.2ml D2O into bottle, weigh, record weight 1.333g

1. Prep a 0.2/5/0.2ml into 1.8ml test tube gamma from the Tank 22 sample (doesn't matter which bottle you use), label Tank 22 Pre CST1216

2. Pipette 6ml of Tank 22 (Gina knows where, was delivered to us last week in 3 green shielded bottles) into the 15ml poly bottles labeled Tk22B20, tk22B20G20, tk22B20G10, tk22B20G5, tk22CSR1216

3. Pipette 6ml of 0.5M NaOH into the 15ml poly bottles labeled CTRLtk221216, BLKtk221216,
4. Prepare a 400 mg/L Glycolate Standard, Pipette 2ml of our 1000 mg/L Glycolate Standard into 3ml DI water

5. We received a 1000 ppm Benzilic acid standard from Tom White (Travis is painfully aware of where this one is)

6. For Tk22B20, add 0.15ml 1000mg/L Benzilic Acid

7. For tk22B20G20, add 0.15ml 1000mg/L Benzilic Acid, and 0.4ml 400 mg/L Glycolate Standard

8. For tk22B20G10, add 0.15ml 1000mg/L Benzilic Acid, and 0.2ml 400 mg/L Glycolate Standard

9. For tk22B20G5, add 0.15ml 1000mg/L Benzilic Acid, and 0.1ml 400 mg/L Glycolate Standard
10. For CTRLtk221216, add 0.15ml 1000mg/L Benzilic Acid, and 0.4ml 400 mg/L Glycolate Standard

11. add 3grams CST, 1g MST (From B-046), cap, shake for 10 seconds
12. Filter off the Resins, decant into new 15ml polybottles
13. add 3grams CST (From B-046), 1g MST, cap, shake for 10 seconds
14. Filter off the Resins, decant into new 15ml polybottles
15. Prep a 0.2ml into 1.8ml Test tube gamma, label tk22 1219 Post
16. Send the CSR samples to Tom White for Glycolate analysis, and the gamma samples to B-003 so we can see how much Cs-137 we removed

DPD

Tank 22 HTF-22-20-91 Error analysis

			scans = 32 9 seconds each					
			HTF-22-20-91					
			standard addition					
			mg/L					
			spike	HNMR Height				
			0	0				
			6.67	5906020				
			13.3	10449324				
			26.6	18867771				
		average	11.6425					
		devsq	386.747675					
	2 sigma error bars on regression (note that only measured points were included!)					Defined values		
	Y = 698560 (X) + 672785					Slope, m	m	698560.8
	assumed x	calculated y	2 sigma	Calc y + 2 sigma	Calc y - 2 sigma	intercept,	b	672785
	-2.917	-322285.738	1364951.875	35.0217176	-2729868.729	Observati	n	4
estimated	0	12335	1183942.398	1856727.398	-511157.398	Se	SYX	763993.5
	0.6751	89778.4214	1144369.794	2288753.19	13.60233315	Average X	XAVG	11.64
	5	585905	921890.4128	5087479.413	3243698.587	SSX	SSX	386.7
	10	1159475	774548.1439	8432941.144	6883844.856		t	2
	15	1733045	807371.2183	11958568.22	10343825.78			
	20	2306615	1002822.169	15646823.17	13641178.83		=t*SYX*SQRT(1/n+(N7-XAVG)^2/SSX)	
	25	2880185	1288928.581	19425733.58	16847876.42		=(m*N7+b)+P7	
	30	3453755	1618302.206	23247911.21	20011306.79		=(m*N7+b)-P7	

Tank 22 HTF-22-20-91 Linear regression for LOQ/LOD

			X	Y							
			calculated								
		measured	linear regressiobn								
		peak height	instrument		peform regression of instrument response in ng (x) to actual ng (y)						
		(counts)	response	actual	see associated spreadsheet for results						
			(mg/L)	(mg/L)	the LOQ = 10 x (Std error on intercept / slope)						
		0	-0.9631	0	the LOD = 3.3 x (Std error on intercept / slope)						
		5906020	7.49146	6.67							
		10449324	13.9953	13.3	**LOQ**		**LOD**				
		18867771	26.0464	26.6	**8.49**		**2.80**				
	used to calculate column E										
	slope	698560									
	intercept	672785									
		Y = 698560 (X) + 672785									

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.996921535
R Square	0.993852548
Adjusted R	0.990778821
Standard E	1.090301094
Observati	4

ANOVA

	df	*SS*	*MS*	*F*	*gnificance F*
Regressio	1	384.370162	384.3702	323.338	0.003078
Residual	2	2.377512953	1.188756		
Total	3	386.747675			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*ower 95.0%*	*pper 95.0%*
Intercept	0.071571786	0.843365109	0.084865	0.940099	-3.55714	3.700279	-3.55714	3.700279
X Variable	0.993851448	0.055270461	17.9816	0.003078	0.756042	1.231661	0.756042	1.231661

RESIDUAL OUTPUT

Observatio	*Predicted Y*	*Residuals*
1	-0.88560919	0.885609195
2	7.516971152	-0.846971152
3	13.98079567	-0.680795674
4	25.95784237	0.642157632

Tank 38 HTF-38-20-103 (45 mL) and HTF 38-20-104 (15 mL) locked SAM experiment with D_2O, benzilic acid, pH adjustment and ion exchange titanates – detail in appendix B (32 scans @ 9 seconds a scan) (section 3.9)

R&D Directions **Reference: PS PL-AP-4006**

1. PI: Thomas White 2. Task Title: Analysis for NMR Tank 38
3. Date: 1/25/2021 Customer Name: FS Analyst: TLW/LC
4. Work Group and Location: Analytical Development, Bldg. 773A, Lab B134
5. Applicable Reference Documents: L1 Manual, AD Procedure 2310 Analysis of Solutions by IC; HAS # SRNL-HA-01236.

Method **NMR (tank 38)**

Prepare NMR tubes for Fernando Fonduer

#	Sample	glycolate, mg/L	Benzilic acid, mg/L	OH, M
1	Tank 38 G0/B20	0.0	19.7	
2	Tank 38 G50/B20	50.0	18.8	
3	Tank 38 G25/B20	25.6	19.2	
4	Tank 38 G13B20	13.0	19.5	
5	Tank 38 G/B	0.0	0.0	
6	Control	50.0	18.8	0.5
7	Blk	0.0	0.0	0.5
8	Tank 38 G5/B20 from 1	5.0	20.0	
9	Tank 38 G1/B20 from 1	1.0	20.0	
10	Tank 38 G20/B20 from 5	20.0	20.0	

Hood

Sample	100 glycolate, mL	1000 Benzilic, mL	Tk 38, mL	V, mL	gly spike, mg/L	benz spike, mg/L
Tank 38 G20/B20 (1000 gly)	0.030	0.030	(S) 1.50	1.56	19.2	19.23
Tank 38 G5/B20	0.080	0.030	(1) 1.50	1.61	5.0	18.63
Tank 38 G1/B20	0.015	0.030	(1) 1.50	1.55	1.0	19.42

5 1 1

✓ Send to Fernando Fonduer

F. Fonduer

Tank 38 samples

Corrosive

Date

7

Tank 38 Error analysis

			32 scans, 9s							
			HTF-38-20-103							
			Example of standard addition							
			mg/L							
			spike	HNMR Height						
			0	0						
			6.20	2261039						
			16.7	4942661						
			33.3	9831356						
			66.7	19559430						
		average	30.7							
		devsq	2098							
	2 sigma error bars on regression (note that only measured points were included!)							Defined values		
	Y =287936(X) + 304178.9							Slope, m	m	287936.3
	assumed x	calculated	2 sigma	Calc y + 2 sigma	Calc y - 2 sigma			intercept, b	b	304178.9
	-2	-271693	300928.7959	29235.15561	-572622.4363			Observati	n	5
estimated	0	304178.9	287831.7857	592010.696	16347.12454			Se	SYX	178535.8
	5	1743859	256314.1462	2000174.433	1487546.141			Average X	XAVG	30.71667
	10	3183539	227124.9984	3410666.662	2956416.665			SSX	SSX	2097.719
	15	4623219	201279.9217	4824502.962	4421943.118	y-intercept			t	2
	20	6062899	180223.3824	6243127.799	5882681.034					
	25	7502579	165790.0687	7668375.862	7336795.724				=t*SYX*SQRT(1/n+(N7-XAVG)^2/SSX)	
	30	8942259	159784.9958	9102052.165	8782482.174				=(m*N7+b)+P7	
	35	10381939	163141.5384	10545090.08	10218807.01				=(m*N7+b)-P7	
	40	11821619	175322.8361	11996952.76	11646307.09					
	45	13261299	194679.3539	13455990.65	13066631.94					
	50	14700979	219319.4553	14920312.13	14481673.22					
	55	16140659	247671.1828	16388345.23	15893002.87					
	60	17580339	278603.7056	17858959.13	17301751.72					
	65	19020019	311348.7649	19331385.57	18708688.04					
	70	20459699	345391.2285	20805109.41	20114326.95					

Tank 38 linear regression for LOQ and LOD

		X	Y								
		calculated									
	measured	linear regressiobn									
	peak height	instrument			peform regression of instrument response in ng (x) to actual ng (y)						
	(counts)	response	actual		see associated spreadsheet for results						
		(mg/L)	(mg/L)		the LOQ = 10 x (Std error on intercept / slope)						
	0	-1.05641	0		the LOD = 3.3 x (Std error on intercept / slope)						
	2261039	6.79617	6.2								
	4942661	16.1094	16.7		**LOQ**		**LOD**				
	9831356	33.0878	33.3		**4.38**		**1.45**				
	19559430	66.8734	66.7								
used to calculate column E											
slope	287936										
intercept	304178										
	Y =287936(X) + 304178.9										

SUMMARY OUTPUT

Regression Statistics	
Multiple F	0.999754713
R Square	0.999509486
Adjusted I	0.999345981
Standard E	0.682936529
Observati	5

ANOVA

	df	*SS*	*MS*	*F*	*gnificance F*
Regressio	1	2851.130571	2851.131	6113.029	4.61E-06
Residual	3	1.399206906	0.466402		
Total	4	2852.529778			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*ower 95.0%*	*pper 95.0%*
Intercept	0.442829215	0.43420382	1.019865	0.382869	-0.939	1.82466	-0.939	1.82466
X Variable	0.990494507	0.012668461	78.18586	4.61E-06	0.950178	1.030811	0.950178	1.030811

RESIDUAL OUTPUT

Observatio	*Predicted Y*	*Residuals*
1	-0.60353747	0.60353747
2	7.174394809	-0.974394809
3	16.39912482	0.267541848
4	33.21614507	0.117188265
5	66.68053944	-0.013872774

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